CHAPTER 17

PROPERTIES OF SOLUTIONS

Solution Composition

12. Mass percent: the percent by mass of the solute in the solution.

Mole fraction: the ratio of the number of moles of a given component to the total number of moles of solution.

Molarity: the number of moles of solute per liter of solution.

Molality: the number of moles of solute per kilogram of solvent.

Volume is temperature-dependent, whereas mass and the number of moles are not. Only molarity has a volume term, so only molarity is temperature-dependent.

13. a. HNO₃(l) → H⁺(aq) + NO₃⁻(aq)  b. Na₂SO₄(s) → 2 Na⁺(aq) + SO₄²⁻(aq)
   c. Al(NO₃)₃(s) → Al³⁺(aq) + 3 NO₃⁻(aq)  d. SrBr₂(s) → Sr²⁺(aq) + 2 Br⁻(aq)
   e. KClO₄(s) → K⁺(aq) + ClO₄⁻(aq)  f. NH₄Br(s) → NH₄⁺(aq) + Br⁻(aq)
   g. NH₄NO₃(s) → NH₄⁺(aq) + NO₃⁻(aq)  h. CuSO₄(s) → Cu²⁺(aq) + SO₄²⁻(aq)
   i. NaOH(s) → Na⁺(aq) + OH⁻(aq)

14. Mol Na₂CO₃ = 0.0700 L × \frac{3.0 \text{ mol Na}_2\text{CO}_3}{L} = 0.21 \text{ mol Na}_2\text{CO}_3

Na₂CO₃(s) → 2 Na⁺(aq) + CO₃²⁻(aq);  \text{ mol Na}^+ = 2(0.21) = 0.42 \text{ mol}

Mol NaHCO₃ = 0.0300 L × \frac{1.0 \text{ mol NaHCO}_3}{L} = 0.030 \text{ mol NaHCO}_3

NaHCO₃(s) → Na⁺(aq) + HCO₃⁻(aq);  \text{ mol Na}^+ = 0.030 \text{ mol}

\frac{M_{\text{Na}^+}}{\text{total volume}} = \frac{0.42 \text{ mol} + 0.030 \text{ mol}}{0.0700 \text{ L} + 0.030 \text{ L}} = \frac{0.45 \text{ mol}}{0.1000 \text{ L}} = 4.5 \text{ M Na}^+
15. Molality = \( \frac{40.0 \text{ g EG}}{60.0 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g}}{62.07 \text{ g}} \times \frac{1 \text{ mol EG}}{62.07 \text{ g}} = 10.7 \text{ mol/kg} \)

\[
\text{Molarity} = \frac{40.0 \text{ g EG}}{100.0 \text{ g solution}} \times \frac{1.05 \text{ g cm}^3}{\text{cm}^3} \times \frac{1000 \text{ cm}^3}{\text{L}} \times \frac{1 \text{ mol}}{62.07 \text{ g}} = 6.77 \text{ mol/L}
\]

\[
40.0 \text{ g EG} \times \frac{1 \text{ mol}}{62.07 \text{ g}} = 0.644 \text{ mol EG; 60.0 g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 3.33 \text{ mol H}_2\text{O}
\]

\[
\chi_{\text{EG}} = \frac{0.644}{3.33 + 0.644} = 0.162 = \text{mole fraction ethylene glycol}
\]

16. Hydrochloric acid (HCl):

\[
\text{molarity} = \frac{38 \text{ g HCl}}{100. \text{ g soln}} \times \frac{1.19 \text{ g soln cm}^3}{\text{cm}^3 \text{ soln}} \times \frac{1000 \text{ cm}^3}{\text{L}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g}} = 12 \text{ mol/L}
\]

\[
\text{molality} = \frac{38 \text{ g HCl}}{62 \text{ g solvent}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol HCl}}{36.5 \text{ g}} = 17 \text{ mol/kg}
\]

\[
38 \text{ g HCl} \times \frac{1 \text{ mol}}{36.5 \text{ g}} = 1.0 \text{ mol HCl; 62 g H}_2\text{O} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 3.4 \text{ mol H}_2\text{O}
\]

\[
\text{mole fraction of HCl} = \chi_{\text{HCl}} = \frac{1.0}{3.4 + 1.0} = 0.23
\]

Nitric acid (HNO\(_3\)):

\[
\frac{70. \text{ g HNO}_3}{100. \text{ g soln}} \times \frac{1.42 \text{ g soln cm}^3}{\text{cm}^3 \text{ soln}} \times \frac{1000 \text{ cm}^3}{\text{L}} \times \frac{1 \text{ mol HNO}_3}{63.0 \text{ g}} = 16 \text{ mol/L}
\]

\[
\frac{70. \text{ g HNO}_3}{30. \text{ g solvent}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol HNO}_3}{63.0 \text{ g}} = 37 \text{ mol/kg}
\]

\[
70. \text{ g HNO}_3 \times \frac{1 \text{ mol}}{63.0 \text{ g}} = 1.1 \text{ mol HNO}_3; 30. \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 1.7 \text{ mol H}_2\text{O}
\]

\[
\chi_{\text{HNO}_3} = \frac{1.1}{1.7 + 1.1} = 0.39
\]
Sulfuric acid (H$_2$SO$_4$):

\[
\frac{95 \text{ g H}_2\text{SO}_4}{100. \text{ g soln}} \times \frac{1.84 \text{ g soln}}{\text{cm}^3 \text{ soln}} \times \frac{1000 \text{ cm}^3}{\text{L}} \times \frac{1 \text{ mol H}_2\text{SO}_4}{98.1 \text{ g H}_2\text{SO}_4} = 18 \text{ mol/L}
\]

\[
\frac{95 \text{ g H}_2\text{SO}_4}{5 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol}}{98.1 \text{ g}} = 194 \text{ mol/kg} \approx 200 \text{ mol/kg}
\]

\[
95 \text{ g H}_2\text{SO}_4 \times \frac{1 \text{ mol}}{98.1 \text{ g}} = 0.97 \text{ mol H}_2\text{SO}_4; \quad 5 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 0.3 \text{ mol H}_2\text{O}
\]

\[
\chi_{\text{H}_2\text{SO}_4} = \frac{0.97}{0.97 + 0.3} = 0.76
\]

Acetic Acid (CH$_3$CO$_2$H):

\[
\frac{99 \text{ g CH}_3\text{CO}_2\text{H}}{100. \text{ g soln}} \times \frac{1.05 \text{ g soln}}{\text{cm}^3 \text{ soln}} \times \frac{1000 \text{ cm}^3}{\text{L}} \times \frac{1 \text{ mol}}{60.05 \text{ g}} = 17 \text{ mol/L}
\]

\[
\frac{99 \text{ g CH}_3\text{CO}_2\text{H}}{1 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol}}{60.05 \text{ g}} = 1600 \text{ mol/kg} \approx 2000 \text{ mol/kg}
\]

\[
99 \text{ g CH}_3\text{CO}_2\text{H} \times \frac{1 \text{ mol}}{60.05 \text{ g}} = 1.6 \text{ mol CH}_3\text{CO}_2\text{H}; \quad 1 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 0.06 \text{ mol H}_2\text{O}
\]

\[
\chi_{\text{CH}_3\text{CO}_2\text{H}} = \frac{1.6}{1.6 + 0.06} = 0.96
\]

Ammonia (NH$_3$):

\[
\frac{28 \text{ g NH}_3}{100. \text{ g soln}} \times \frac{0.90 \text{ g}}{\text{cm}^3 \text{ soln}} \times \frac{1000 \text{ cm}^3}{\text{L}} \times \frac{1 \text{ mol}}{17.0 \text{ g}} = 15 \text{ mol/L}
\]

\[
\frac{28 \text{ g NH}_3}{72 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol}}{17.0 \text{ g}} = 23 \text{ mol/kg}
\]

\[
28 \text{ g NH}_3 \times \frac{1 \text{ mol}}{17.0 \text{ g}} = 1.6 \text{ mol NH}_3; \quad 72 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 4.0 \text{ mol H}_2\text{O}
\]

\[
\chi_{\text{NH}_3} = \frac{1.6}{4.0 + 1.6} = 0.29
\]

17. \quad 25 \text{ mL C}_5\text{H}_12 \times \frac{0.63 \text{ g}}{\text{mL}} = 16 \text{ g C}_5\text{H}_12; \quad 25 \text{ mL} \times \frac{0.63 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{72.15 \text{ g}} = 0.22 \text{ mol C}_5\text{H}_12
45 mL C₆H₁₄ × \frac{0.66 \text{ g}}{\text{mL}} = 30. \text{ g C₆H₁₄}; \ 45 \text{ mL} \times \frac{0.66 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{86.17 \text{ g}} = 0.34 \text{ mol C₆H₁₄}

\text{Mass % pentane} = \frac{\text{mass pentane}}{\text{total mass}} \times 100 = \frac{16 \text{ g}}{16 \text{ g} + 30. \text{ g}} \times 100 = 35\%

\chi_{\text{pentane}} = \frac{\text{mol pentane}}{\text{total mol}} = \frac{0.22 \text{ mol}}{0.22 \text{ mol} + 0.34 \text{ mol}} = 0.39

\text{Molality} = \frac{\text{mol pentane}}{\text{kg hexane}} = \frac{0.22 \text{ mol}}{0.030 \text{ kg}} = 7.3 \text{ mol/kg}

\text{Molarity} = \frac{\text{mol pentane}}{\text{L solution}} = \frac{0.22 \text{ mol}}{25 \text{ mL} + 45 \text{ mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 3.1 \text{ mol/L}

18. If we have 100.0 mL of wine:

12.5 mL C₂H₅OH × \frac{0.789 \text{ g}}{\text{mL}} = 9.86 \text{ g C₂H₅OH and } 87.5 \text{ mL H₂O} \times \frac{1.00 \text{ g}}{\text{mL}} = 87.5 \text{ g H₂O}

\text{Mass % ethanol} = \frac{9.86 \text{ g}}{87.5 \text{ g} + 9.86 \text{ g}} \times 100 = 10.1\% \text{ by mass}

\text{Molality} = \frac{9.86 \text{ g C₂H₅OH}}{0.0875 \text{ kg H₂O}} \times \frac{1 \text{ mol}}{46.07 \text{ g}} = 2.45 \text{ mol/kg}

19. If we have 1.00 L of solution:

1.37 \text{ mol citric acid} \times \frac{192.1 \text{ g}}{\text{mol}} = 263 \text{ g citric acid}

1.00 \times 10^3 \text{ mL solution} \times \frac{1.10 \text{ g}}{\text{mL}} = 1.10 \times 10^3 \text{ g solution}

\text{Mass % of citric acid} = \frac{263 \text{ g}}{1.10 \times 10^3 \text{ g}} \times 100 = 23.9\%

In 1.00 L of solution, we have 263 g citric acid and (1.10 \times 10^3 - 263) = 840 g of \text{H₂O}.

\text{Molality} = \frac{1.37 \text{ mol citric acid}}{0.84 \text{ kg H₂O}} = 1.6 \text{ mol/kg}

840 \text{ g H₂O} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 47 \text{ mol H₂O}; \ \chi_{\text{citric acid}} = \frac{1.37}{47 + 1.37} = 0.028
20. \[
\frac{1.00 \text{ mol acetone}}{1.00 \text{ kg ethanol}} = 1.00 \text{ molal; } 1.00 \times 10^3 \text{ g C}_2\text{H}_5\text{OH} \times \frac{1 \text{ mol}}{46.07 \text{ g}} = 21.7 \text{ mol C}_2\text{H}_5\text{OH}
\]

\[\chi_{acetone} = \frac{1.00}{1.00 + 21.7} = 0.0441\]

\[
1 \text{ mol CH}_3\text{COCH}_3 \times \frac{58.08 \text{ g CH}_3\text{COCH}_3}{\text{mol CH}_3\text{COCH}_3} \times \frac{1 \text{ mL}}{0.788 \text{ g}} = 73.7 \text{ mL CH}_3\text{COCH}_3
\]

\[1.00 \times 10^3 \text{ g ethanol} \times \frac{1 \text{ mL}}{0.789 \text{ g}} = 1270 \text{ mL; total volume} = 1270 + 73.7 = 1340 \text{ mL}\]

\[\text{Molarity} = \frac{1.00 \text{ mol}}{1.34 \text{ L}} = 0.746 \text{ M}\]

21. Because the density of water is 1.00 g/mL, 100.0 mL of water has a mass of 100. g.

\[\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{10.0 \text{ g H}_3\text{PO}_4 + 100. \text{ g H}_2\text{O}}{104 \text{ mL}} = 1.06 \text{ g/mL} = 1.06 \text{ g/cm}^3\]

\[\text{Mol H}_3\text{PO}_4 = 10.0 \text{ g} \times \frac{1 \text{ mol}}{97.99 \text{ g}} = 0.102 \text{ mol H}_3\text{PO}_4\]

\[\text{Mol H}_2\text{O} = 100. \text{ g} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 5.55 \text{ mol H}_2\text{O}\]

\[\text{Mole fraction of H}_3\text{PO}_4 = \frac{0.102 \text{ mol H}_3\text{PO}_4}{(0.102 + 5.55) \text{ mol}} = 0.0180\]

\[\chi_{H_2O} = 1.0000 - 0.0180 = 0.9820\]

\[\text{Molarity} = \frac{0.102 \text{ mol H}_3\text{PO}_4}{0.104 \text{ L soln}} = 0.981 \text{ mol/L}\]

\[\text{Molality} = \frac{0.102 \text{ mol H}_3\text{PO}_4}{0.100 \text{ kg solvent}} = 1.02 \text{ mol/kg}\]

22. a. If we use 100. mL (100. g) of H\text{2O}, we need:

\[0.100 \text{ kg H}_2\text{O} \times \frac{2.0 \text{ mol KCl}}{\text{kg}} \times \frac{74.55 \text{ g}}{\text{mol KCl}} = 14.9 \text{ g} = 15 \text{ g KCl}\]
Dissolve 15 g KCl in 100. mL H₂O to prepare a 2.0 \textit{m} KCl solution. This will give us slightly more than 100 mL, but this will be the easiest way to make the solution. Because we don’t know the density of the solution, we can’t calculate the molarity and use a volumetric flask to make exactly 100 mL of solution.

b. If we took 15 g NaOH and 85 g H₂O, the volume would probably be less than 100 mL. To make sure we have enough solution, let’s use 100. mL H₂O (100. g H₂O). Let $x = \text{mass of NaCl}$.

\[
\text{Mass \%} = 15 = \frac{x}{100. + x} \times 100, \quad 1500 + 15x = (100.)x, \quad x = 17.6 \text{ g} \approx 18 \text{ g}
\]

Dissolve 18 g NaOH in 100. mL H₂O to make a 15% NaOH solution by mass.

c. In a fashion similar to part b, let’s use 100. mL CH₃OH. Let $x = \text{mass of NaOH}$.

\[
100. \text{ mL CH₃OH} \times \frac{0.79 \text{ g}}{\text{mL}} = 79 \text{ g CH₃OH}
\]

\[
\text{Mass \%} = 25 = \frac{x}{79 + x} \times 100, \quad 25(79) + 25x = (100.)x, \quad x = 26.3 \text{ g} \approx 26 \text{ g}
\]

Dissolve 26 g NaOH in 100. mL CH₃OH.

d. To make sure we have enough solution, let’s use 100. mL (100. g) of H₂O. Let $x = \text{mol C₆H₁₂O₆}$.

\[
100. \text{ g H₂O} \times \frac{1 \text{ mol H₂O}}{18.02 \text{ g}} = 5.55 \text{ mol H₂O}
\]

\[
\chi_{C₆H₁₂O₆} = 0.10 = \frac{x}{x + 5.55}, \quad (0.10)x + 0.56 = x, \quad x = 0.62 \text{ mol C₆H₁₂O₆}
\]

\[
0.62 \text{ mol C₆H₁₂O₆} \times \frac{180.2 \text{ g}}{\text{mol}} = 110 \text{ g C₆H₁₂O₆}
\]

Dissolve 110 g C₆H₁₂O₆ in 100. mL of H₂O to prepare a solution with $\chi_{C₆H₁₂O₆} = 0.10$.

**Thermodynamics of Solutions and Solubility**

23. “Like dissolves like” refers to the nature of the intermolecular forces. Polar solutes and ionic solutes dissolve in polar solvents because the types of intermolecular forces present in solute and solvent are similar. When they dissolve, the strengths of the intermolecular forces in solution are about the same as in pure solute and pure solvent. The same is true for nonpolar solutes in nonpolar solvents. The strengths of the intermolecular forces (London dispersion forces) are about the same in solution as in pure solute and pure solvent. In all cases of like dissolves like, the magnitude of $\Delta H_{\text{soln}}$ is either a small positive number (endothermic) or a
small negative number (exothermic), with a value close to zero. For polar solutes in nonpolar solvents and vice versa, \( \Delta H_{\text{soln}} \) is a very large, unfavorable value (very endothermic). Because the energetics are so unfavorable, polar solutes do not dissolve in nonpolar solvents, and vice versa.

24. The dissolving of an ionic solute in water can be thought of as taking place in two steps. The first step, called the lattice energy term, refers to breaking apart the ionic compound into gaseous ions. This step, as indicated in the problem requires a lot of energy and is unfavorable. The second step, called the hydration energy term, refers to the energy released when the separated gaseous ions are stabilized as water molecules surround the ions. Because the interactions between water molecules and ions are strong, a lot of energy is released when ions are hydrated. Thus the dissolution process for ionic compounds can be thought of as consisting of an unfavorable and a favorable energy term. These two processes basically cancel each other out, so when ionic solids dissolve in water, the heat released or gained is minimal, and the temperature change is minimal.

25. Using Hess’s law:

\[
\text{NaI}(s) \rightarrow \text{Na}^+(g) + \Gamma(g) \quad \Delta H = -\Delta H_{\text{LE}} = -(-686 \text{ kJ/mol})
\]

\[
\text{Na}^+(g) + \Gamma(g) \rightarrow \text{Na}^+(aq) + \Gamma(aq) \quad \Delta H = \Delta H_{\text{hyd}} = -694 \text{ kJ/mol}
\]

\[
\text{NaI}(s) \rightarrow \text{Na}^+(aq) + \Gamma(aq) \quad \Delta H_{\text{soln}} = -8 \text{ kJ/mol}
\]

\( \Delta H_{\text{soln}} \) refers to the heat released or gained when a solute dissolves in a solvent. Here, an ionic compound dissolves in water.

26. a. \[
\text{CaCl}_2(s) \rightarrow \text{Ca}^{2+}(g) + 2 \text{Cl}^-(g) \quad \Delta H = -\Delta H_{\text{LE}} = -(-2247 \text{ kJ})
\]

\[
\text{Ca}^{2+}(g) + 2 \text{Cl}^-(g) \rightarrow \text{Ca}^{2+}(aq) + 2 \text{Cl}^-(aq) \quad \Delta H = \Delta H_{\text{hyd}}
\]

\[
-46 \text{ kJ} = 2247 \text{ kJ} + \Delta H_{\text{hyd}}, \quad \Delta H_{\text{hyd}} = -2293 \text{ kJ}
\]

b. The enthalpy of hydration for \( \text{CaCl}_2 \) is more exothermic than for \( \text{CaI}_2 \). Any differences must be due to differences in hydrations between \( \text{Cl}^- \) and \( \Gamma^- \). Thus the chloride ion is more strongly hydrated than the iodide ion.

27. Both \( \text{Al(OH)}_3 \) and \( \text{NaOH} \) are ionic compounds. Because the lattice energy is proportional to the charge of the ions, the lattice energy of aluminum hydroxide is greater than that of sodium hydroxide. The attraction of water molecules for \( \text{Al}^{3+} \) and \( \text{OH}^- \) cannot overcome the larger lattice energy, and \( \text{Al(OH)}_3 \) is insoluble. For \( \text{NaOH} \), the favorable hydration energy is large enough to overcome the smaller lattice energy, and \( \text{NaOH} \) is soluble.
28. a. Mg$^{2+}$; smaller size, higher charge  
    b. Be$^{2+}$; smaller size  
    c. Fe$^{3+}$; smaller size, higher charge  
    d. F$^{-}$; smaller size  
    e. Cl$^{-}$; smaller size  
    f. SO$_4^{2-}$; higher charge  

29. Water is a polar molecule capable of hydrogen bonding. Polar molecules, especially molecules capable of hydrogen bonding, and ions can be hydrated. For covalent compounds, as polarity increases, the attraction to water (hydration) increases. For ionic compounds, as the charge of the ions increase and/or the size of the ions decrease, the attraction to water (hydration) increases.  

    a. CH$_3$CH$_2$OH; CH$_3$CH$_2$OH is polar, whereas CH$_3$CH$_2$CH$_3$ is nonpolar.  
    b. CHCl$_3$; CHCl$_3$ is polar, whereas CCl$_4$ is nonpolar.  
    c. CH$_3$CH$_2$OH; CH$_3$CH$_2$OH is much more polar than CH$_3$(CH$_2$)$_{14}$CH$_2$OH.  

30. Water is a polar solvent and dissolves polar solutes and ionic solutes. Carbon tetrachloride (CCl$_4$) is a nonpolar solvent and dissolves nonpolar solutes (like dissolve like). To predict the polarity of the following molecules, draw the correct Lewis structure and then determine if the individual bond dipoles cancel or not. If the bond dipoles are arranged in such a manner that they cancel each other out, then the molecule is nonpolar. If the bond dipoles do not cancel each other out, then the molecule is polar.  

    a. KrF$_2$, $8 + 2(7) = 22$ e$^-$  
       nonpolar; soluble in CCl$_4$  
    b. SF$_2$, $6 + 2(7) = 20$ e$^-$  
       polar; soluble in H$_2$O  
    c. SO$_2$, $6 + 2(6) = 18$ e$^-$  
       + 1 more  
       polar; soluble in H$_2$O  
    d. CO$_2$, $4 + 2(6) = 16$ e$^-$  
       nonpolar; soluble in CCl$_4$  
    e. MgF$_2$ is an ionic compound so it is soluble in water.
31. As the length of the hydrocarbon chain increases, the solubility decreases. The –OH end of the alcohols can hydrogen-bond with water. The hydrocarbon chain, however, is basically nonpolar and interacts poorly with water. As the hydrocarbon chain gets longer, a greater portion of the molecule cannot interact with the water molecules, and the solubility decreases; i.e., the effect of the –OH group decreases as the alcohols get larger.

32. The main intermolecular forces are:

hexane (C\textsubscript{6}H\textsubscript{14}): London dispersion; chloroform (CHCl\textsubscript{3}): dipole-dipole, London dispersion; methanol (CH\textsubscript{3}OH): H-bonding; and H\textsubscript{2}O: H-bonding (two places)

There is a gradual change in the nature of the intermolecular forces (weaker to stronger). Each preceding solvent is miscible in its predecessor because there is not a great change in the strengths of the intermolecular forces from one solvent to the next.

33. Structure effects refer to solute and solvent having similar polarities in order for solution formation to occur. Hydrophobic solutes are mostly nonpolar substances that are “water-fearing.” Hydrophilic solutes are mostly polar or ionic substances that are “water-loving.” Pressure has little effect on the solubilities of solids or liquids; it does significantly affect the solubility of a gas. Henry’s law states that the amount of a gas dissolved in a solution is directly proportional to the pressure of the gas above the solution (C = kP). The equation for Henry’s law works best for dilute solutions of gases that do not dissociate in or react with the solvent. HCl(g) does not follow Henry’s law because it dissociates into H\textsuperscript{+}(aq) and Cl\textsuperscript{−}(aq) in solution (HCl is a strong acid). For O\textsubscript{2} and N\textsubscript{2}, Henry’s law works well since these gases do not react with the water solvent.

An increase in temperature can either increase or decrease the solubility of a solid solute in water. It is true that a solute dissolves more rapidly with an increase in temperature, but the amount of solid solute that dissolves to form a saturated solution can either decrease or increase with temperature. The temperature effect is difficult to predict for solid solutes. However, the temperature effect for gas solutes is easier to predict because the solubility of a gas typically decreases with increasing temperature.

34. Henry’s law is obeyed most accurately for dilute solutions of gases that do not dissociate in or react with the solvent. O\textsubscript{2} will bind to hemoglobin in the blood. Given this reaction in the solvent, O\textsubscript{2}(g) in blood does not follow Henry’s law.
35. \( P_{\text{gas}} = kC \), \( 0.790 \text{ atm} = k \times \frac{8.21 \times 10^{-4} \text{ mol}}{L} \), \( k = 962 \text{ L atm/mol} \)

\[ P_{\text{gas}} = kC \], \( 1.10 \text{ atm} = \frac{962 \text{ L atm}}{\text{mol}} \times C \), \( C = 1.14 \times 10^{-3} \text{ mol/L} \)

36. 750. mL grape juice \( \times \frac{12 \text{ mL } C_2H_5OH}{100. \text{ mL juice}} \times \frac{0.79 \text{ g } C_2H_5OH}{\text{mL}} \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g}} \)

\[ \times \frac{2 \text{ mol } CO_2}{2 \text{ mol } C_2H_5OH} = 1.54 \text{ mol } CO_2 \] (carry extra significant figure)

1.54 mol CO\(_2\) = total mol CO\(_2\) = mol CO\(_2\)(g) + mol CO\(_2\)(aq) = \( n_g + n_{aq} \)

\[ P_{CO_2} = \frac{n_gRT}{V} = \frac{n_g \left( \frac{0.08206 \text{ L atm}}{\text{mol K}} \right) (298 \text{ K})}{75 \times 10^{-3} \text{ L}} = 326n_g \]

\[ P_{CO_2} = kC = \frac{32 \text{ L atm}}{\text{mol}} \times \frac{n_{aq}}{0.750 \text{ L}} = (42.7)n_{aq} \]

\[ P_{CO_2} = 326n_g = (42.7)n_{aq} \] and from above \( n_{aq} = 1.54 - n_g \); solving:

\[ 326n_g = 42.7(1.54 - n_g), \ 369n_g = 65.8, \ n_g = 0.18 \text{ mol} \]

\[ P_{CO_2} = 326(0.18) = 59 \text{ atm in gas phase}; \ 59 \text{ atm} = \frac{32 \text{ L atm}}{\text{mol}} \times C, \ C = 1.8 \text{ mol } CO_2/\text{L in wine} \]

37. As the temperature increases the gas molecules will have a greater average kinetic energy. A greater fraction of the gas molecules in solution will have a kinetic energy greater than the attractive forces between the gas molecules and the solvent molecules. More gas molecules are able to escape to the vapor phase and the solubility of the gas decreases.

Vapor Pressures of Solution

38. \( \text{Mol } C_3H_6O_3 = 164 \text{ g} \times \frac{1 \text{ mol}}{92.09 \text{ g}} = 1.78 \text{ mol } C_3H_6O_3 \)

\( \text{Mol } H_2O = 338 \text{ mL} \times \frac{0.992 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 18.6 \text{ mol } H_2O \)

\[ P_{\text{soln}} = \chi_{H_2O}P_{H_2O}^o = \frac{18.6 \text{ mol}}{(1.78 + 18.6) \text{ mol}} \times 54.74 \text{ torr} = 0.913 \times 54.74 \text{ torr} = 50.0 \text{ torr} \]
CHAPTER 17  PROPERTIES OF SOLUTIONS

39.  
\[ P_{\text{soln}} = \chi_{C_2H_5OH} P_{C_2H_5OH}^o \]  
\[ \chi_{C_2H_5OH} = \frac{\text{mol } C_2H_5OH \text{ in solution}}{\text{total mol in solution}} \]

\[ 53.6 \text{ g } C_3H_8O_3 \times \frac{1 \text{ mol } C_3H_8O_3}{92.09 \text{ g}} = 0.582 \text{ mol } C_3H_8O_3 \]

\[ 133.7 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g}} = 2.90 \text{ mol } C_2H_5OH; \text{ total mol} = 0.582 + 2.90 = 3.48 \text{ mol} \]

\[ 113 \text{ torr} = \frac{2.90 \text{ mol}}{3.48 \text{ mol}} \times P_{C_2H_5OH}^o, \quad P_{C_2H_5OH}^o = 136 \text{ torr} \]

40. Compared to \( H_2O \), solution d (methanol-water) will have the highest vapor pressure since methanol is more volatile than water (\( P_{H_2O}^o = 23.8 \text{ torr at } 25^\circ C \)). Both solution b (glucose-water) and solution c (NaCl-water) will have a lower vapor pressure than water by Raoult's law. NaCl dissolves to give \( Na^+ \) ions and \( Cl^- \) ions; glucose is a nonelectrolyte. Because there are more solute particles in solution c, the vapor pressure of solution c will be the lowest.

41. Solution d (methanol-water): methanol is more volatile than water, which will increase the total vapor pressure to a value greater than the vapor pressure of pure water at this temperature.

42.  
\[ P_{\text{total}} = P_{C_2H_5Cl} + P_{C_2H_5Br}; \quad P = \chi^L P^o; \quad \chi^L = \frac{0.0300 \text{ mol } CH_2Cl_2}{0.0800 \text{ mol total} } = 0.375 \]

\[ P_{\text{total}} = 0.375(133 \text{ torr}) + (1.000 - 0.375)(11.4 \text{ torr}) = 49.9 + 7.13 = 57.0 \text{ torr} \]

In the vapor:  
\[ \chi^V_{C_2H_5Cl_2} = \frac{P_{C_2H_5Cl_2}}{P_{\text{total}}} = \frac{49.9 \text{ torr}}{57.0 \text{ torr}} = 0.875; \quad \chi^V_{C_2H_5Br_2} = 1.000 - 0.875 = 0.125 \]

Note: In the Solutions Guide we added \( V \) or \( L \) to the mole fraction symbol to emphasize which value we are solving. If the \( L \) or \( V \) is omitted, then the liquid phase is assumed.

43.  
\[ P_B = \chi_B P_B^o, \quad \chi_B = \frac{P_B}{P_B^o} = 0.900 \text{ atm}/0.930 \text{ atm} = 0.968 \]

\[ 0.968 = \frac{\text{mol benzene}}{\text{total mol}}; \quad \text{mol benzene} = 78.11 \text{ g } C_6H_6 \times \frac{1 \text{ mol}}{78.11 \text{ g}} = 1.000 \text{ mol} \]

Let \( x = \text{mol solute} \); then:  
\[ \chi_B = 0.968 = \frac{1.000 \text{ mol}}{1.000 + x}, \quad 0.968 + (0.968)x = 1.000, \quad x = 0.033 \text{ mol} \]

Molar mass = \[ \frac{10.0 \text{ g}}{0.033 \text{ mol} } = 303 \text{ g/mol} \approx 3.0 \times 10^2 \text{ g/mol} \]

44.  
\[ P_{CS_2} = \chi^V_{CS_2} P_{\text{total}} = 0.855(263 \text{ torr}) = 225 \text{ torr} \]
\[ P_{CS_2} = \chi_{CS_2}^L P_{CS_2}^o, \quad \chi_{CS_2} = \frac{P_{CS_2}}{P_{CS_2}^o} = \frac{225 \text{ torr}}{375 \text{ torr}} = 0.600 \]

45. a. 25 mL \( \text{C}_5\text{H}_{12} \times \frac{0.63 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{72.15} = 0.22 \text{ mol C}_5\text{H}_{12} \)

45 mL \( \text{C}_6\text{H}_{14} \times \frac{0.66 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol}}{86.17} = 0.34 \text{ mol C}_6\text{H}_{14}; \) total mol = 0.22 + 0.34 = 0.56 mol

\[ \chi_{\text{pen}}^L = \frac{\text{mol pentane in solution}}{\text{total mol in solution}} = \frac{0.22}{0.56} = 0.39, \quad \chi_{\text{hex}}^L = 1.00 - 0.39 = 0.61 \]

\[ P_{\text{pen}} = \chi_{\text{pen}}^L P_{\text{pen}}^o = 0.39(511 \text{ torr}) = 2.0 \times 10^2 \text{ torr}; \quad P_{\text{hex}} = 0.61(150. \text{ torr}) = 92 \text{ torr} \]

\[ P_{\text{total}} = P_{\text{pen}} + P_{\text{hex}} = 2.0 \times 10^2 + 92 = 292 \text{ torr} = 290 \text{ torr} \]

b. From Chapter 5 on gases, the partial pressure of a gas is proportional to the number of moles of gas present. For the vapor phase:

\[ \chi_{\text{pen}}^V = \frac{\text{mol pentane in vapor}}{\text{total mol vapor}} = \frac{P_{\text{pen}}}{P_{\text{total}}} = \frac{2.0 \times 10^2 \text{ torr}}{290 \text{ torr}} = 0.69 \]

Note: In the Solutions Guide, we added V or L to the mole fraction symbol to emphasize which value we are solving. If the L or V is omitted, then the liquid phase is assumed.

46. \( P_{\text{tol}} = \chi_{\text{tol}}^L P_{\text{tol}}^o, \quad P_{\text{pen}} = \chi_{\text{ben}}^L P_{\text{ben}}^o; \) for the vapor, \( \chi_{\text{A}}^V = P_{\text{A}}/P_{\text{total}}. \) Because the mole fractions of benzene and toluene are equal in the vapor phase, \( P_{\text{tol}} = P_{\text{ben}}. \)

\[ \chi_{\text{tol}}^L P_{\text{tol}}^o = \chi_{\text{ben}}^L P_{\text{ben}}^o = (1.00 - \chi_{\text{tol}}^L)P_{\text{ben}}^o, \quad \chi_{\text{tol}}^L(28 \text{ torr}) = (1.00 - \chi_{\text{tol}}^L)95 \text{ torr} \]

123 \( \chi_{\text{tol}}^L = 95, \chi_{\text{tol}}^L = 0.77; \quad \chi_{\text{ben}}^L = 1.00 - 0.77 = 0.23 \]

47. \( P_{\text{total}} = P_{\text{meth}} + P_{\text{prop}}, \) 174 torr = \( \chi_{\text{meth}}^L(303 \text{ torr}) + \chi_{\text{prop}}^L(44.6 \text{ torr}); \quad \chi_{\text{prop}}^L = 1.00 - \chi_{\text{meth}}^L \)

174 = 303 \( \chi_{\text{meth}}^L + (1.00 - \chi_{\text{meth}}^L)44.6 \text{ torr}, \quad \frac{129}{258} = \chi_{\text{meth}}^L = 0.500 \)

\( \chi_{\text{prop}}^L = 1.00 - 0.500 = 0.500 \]

48. An ideal liquid-liquid solution follows Raoul’ts law:

\[ P_{\text{total}} = \chi_A P_A^o + \chi_B P_B^o \]
A nonideal liquid-liquid solution does not follow Raoult’s law, giving a total pressure either greater than predicted by Raoult’s law (positive deviation) or less than predicted (negative deviation).

In an ideal solution, the strengths of the intermolecular forces in solution are equal to the strengths of the intermolecular forces in pure solute and pure solvent. When this is true, $\Delta H_{\text{soln}} = 0$ and $\Delta T_{\text{soln}} = 0$. For positive deviations from Raoult’s law, the solution has weaker intermolecular forces in solution than in pure solute and pure solvent. Positive deviations have $\Delta H_{\text{soln}} > 0$ (are endothermic) and $\Delta T_{\text{soln}} < 0$. For negative deviations, the solution has stronger intermolecular forces in solution than in pure solute or pure solvent. Negative deviations have $\Delta H_{\text{soln}} < 0$ (are exothermic) and $\Delta T_{\text{soln}} > 0$. Examples of each type of solution are:

- ideal: benzene-toluene
- positive deviations: ethanol-hexane
- negative deviations: acetone-water

49. 50.0 g CH$_3$COCH$_3$ $\times \frac{1\text{ mol}}{58.08\text{ g}}$ = 0.861 mol acetone

50.0 g CH$_3$OH $\times \frac{1\text{ mol}}{32.04\text{ g}}$ = 1.56 mol methanol

$$\chi^L_{\text{acetone}} = \frac{0.861}{0.861 + 1.56} = 0.356; \ \chi^L_{\text{methanol}} = 1.000 - \chi^L_{\text{acetone}} = 0.644$$

$$P_{\text{total}} = P_{\text{methanol}} + P_{\text{acetone}} = 0.644(143\text{ torr}) + 0.356(271\text{ torr}) = 92.1\text{ torr} + 96.5\text{ torr} = 188.6\text{ torr}$$

Because partial pressures are proportional to the moles of gas present, in the vapor phase:

$$\chi^v_{\text{acetone}} = \frac{P_{\text{acetone}}}{P_{\text{total}}} = \frac{96.5\text{ torr}}{188.6\text{ torr}} = 0.512; \ \chi^v_{\text{methanol}} = 1.000 - 0.512 = 0.488$$

The actual vapor pressure of the solution (161 torr) is less than the calculated pressure assuming ideal behavior (188.6 torr). Therefore, the solution exhibits negative deviations from Raoult’s law. This occurs when the solute-solvent interactions are stronger than in pure solute and pure solvent.

50. a. An ideal solution would have a vapor pressure at any mole fraction of H$_2$O between that of pure propanol and pure water (between 74.0 torr and 71.9 torr). The vapor pressures of the various solutions are not between these limits, so water and propanol do not form ideal solutions.

b. From the data, the vapor pressures of the various solutions are greater than if the solutions behaved ideally (positive deviation from Raoult’s law). This occurs when the intermolecular forces in solution are weaker than the intermolecular forces in pure solvent and pure solute. This gives rise to endothermic (positive) $\Delta H_{\text{soln}}$ values.
c. The interactions between propanol and water molecules are weaker than between the pure substances because the solutions exhibit a positive deviation from Raoult’s law.

d. At $\chi_{H,O} = 0.54$, the vapor pressure is highest as compared to the other solutions. Because a solution boils when the vapor pressure of the solution equals the external pressure, the $\chi_{H,O} = 0.54$ solution should have the lowest normal boiling point; this solution will have a vapor pressure equal to 1 atm at a lower temperature as compared to the other solutions.

51. No, the solution is not ideal. For an ideal solution, the strengths of intermolecular forces in the solution are the same as in pure solute and pure solvent. This results in $\Delta H_{\text{soln}} = 0$ for an ideal solution. $\Delta H_{\text{soln}}$ for methanol-water is not zero. Because $\Delta H_{\text{soln}} < 0$, this solution exhibits negative deviation from Raoult’s law.

52. Because the solute is volatile, both the water and solute will transfer back and forth between the two beakers. The volume in each beaker will become constant when the concentrations of solute in the beakers are equal to each other. Because the solute is less volatile than water, one would expect there to be a larger net transfer of water molecules into the right beaker than the net transfer of solute molecules into the left beaker. This results in a larger solution volume in the right beaker when equilibrium is reached, i.e., when the solute concentration is identical in each beaker.

53. Solutions of A and B have vapor pressures less than ideal (see Figure 17.11 of the text), so this plot shows negative deviations from Raoul’s law. Negative deviations occur when the intermolecular forces are stronger in solution than in pure solvent and solute. This results in an exothermic enthalpy of solution. The only statement that is false is e. A substance boils when the vapor pressure equals the external pressure. Because $\chi_B = 0.6$ has a lower vapor pressure at the temperature of the plot than either pure A or pure B, one would expect this solution to require the highest temperature in order for the vapor pressure to reach the external pressure. Therefore, the solution with $\chi_B = 0.6$ will have a higher boiling point than either pure A or pure B. (Note that because $P_B^o > P_A^o$, B is more volatile than A.)

**Colligative Properties**

54. Colligative properties are properties of a solution that depend only on the number, not the identity, of the solute particles. A solution of some concentration of glucose ($C_6H_{12}O_6$) has the same colligative properties as a solution of sucrose ($C_{12}H_{22}O_{11}$) having the same concentration.

A substance freezes when the vapor pressure of the liquid and solid are identical to each other. Adding a solute to a substance lowers the vapor pressure of the liquid. A lower temperature is needed to reach the point where the vapor pressures of the solution and solid are identical. Hence the freezing point is depressed when a solution forms.

A substance boils when the vapor pressure of the liquid equals the external pressure. Because a solute lowers the vapor pressure of the liquid, a higher temperature is needed to reach the
point where the vapor pressure of the liquid equals the external pressure. Hence the boiling point is elevated when a solution forms.

55. Osmotic pressure: the pressure that must be applied to a solution to stop osmosis; osmosis is the flow of solvent into the solution through a semipermeable membrane. The equation to calculate osmotic pressure $\pi$ is:

$$\pi = MRT$$

where $M$ is the molarity of the solution, $R$ is the gas constant, and $T$ is the Kelvin temperature. The molarity of a solution approximately equals the molality of the solution when 1 kg solvent $\approx$ 1 L solution. This occurs for dilute solutions of water because $d_{H_2O} = 1.00$ g/cm$^3$.

56. This is true if the solute will dissolve in camphor. Camphor has the largest $K_b$ and $K_f$ constants. This means that camphor shows the largest change in boiling point and melting point as a solute is added. The larger the change in $\Delta T$, the more precise is the measurement, and the more precise is the calculated molar mass. However, if the solute won’t dissolve in camphor, then camphor is no good, and another solvent must be chosen that will dissolve the solute.

57. Molality = $m = \frac{\text{mol solute}}{\text{kg solvent}} = \frac{27.0 \text{ g N}_2\text{H}_4\text{CO}}{150.0 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol N}_2\text{H}_4\text{CO}}{60.06 \text{ g N}_2\text{H}_4\text{CO}} = 3.00 \text{ molal}$

$$\Delta T_b = K_b m = \frac{0.51 \degree C}{\text{molal}} \times 3.00 \text{ molal} = 1.5 \degree C$$

The boiling point is raised from 100.0°C to 101.5°C (assuming $P = 1$ atm).

58. $\Delta T_f = K_f m, \quad \Delta T_f = 1.50 \degree C = \frac{1.86 \degree C}{\text{molal}} \times m, \quad m = 0.806 \text{ mol/kg}$

$$0.200 \text{ kg H}_2\text{O} \times \frac{0.806 \text{ mol C}_3\text{H}_8\text{O}_3}{\text{kg H}_2\text{O}} \times \frac{92.09 \text{ g C}_3\text{H}_8\text{O}_3}{\text{mol C}_3\text{H}_8\text{O}_3} = 14.8 \text{ g C}_3\text{H}_8\text{O}_3$$

59. Molality = $m = \frac{50.0 \text{ g C}_2\text{H}_6\text{O}_2}{50.0 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{1 \text{ mol}}{62.07 \text{ g}} = 16.1 \text{ mol/kg}$

$$\Delta T_f = K_f m = 1.86 \degree C/\text{molal} \times 16.1 \text{ molal} = 29.9 \degree C; \quad T_f = 0.0 \degree C - 29.9 \degree C = -29.9 \degree C$$

$$\Delta T_b = K_b m = 0.51 \degree C/\text{molal} \times 16.1 \text{ molal} = 8.2 \degree C; \quad T_b = 100.0 \degree C + 8.2 \degree C = 108.2 \degree C$$

60. $\Delta T = 25.50 \degree C - 24.59 \degree C = 0.91 \degree C = K_b m, \quad m = \frac{0.91 \degree C}{9.1 \degree C/\text{molal}} = 0.10 \text{ mol/kg}$
Mass \( H_2O \) = 0.0100 kg \( \text{t-butanol} \)

\[
\left( \frac{0.10 \text{ mol} \ H_2O}{\text{kg t-butanol}} \right) \left( \frac{18.02 \text{ g} \ H_2O}{\text{mol} \ H_2O} \right) = 0.018 \text{ g} \ H_2O
\]

61. \( m = \frac{24.0 \text{ g} \times \frac{1 \text{ mol}}{58.0 \text{ g}}}{0.600 \text{ kg}} = 0.690 \text{ mol/kg} \); \( \Delta T_b = K_b m = 0.51°C \text{ kg/mol} \times 0.690 \text{ mol/kg} = 0.35°C \)

\( T_b = 99.725°C + 0.35°C = 100.08°C \)

62. \( \pi = MRT, \ M = \frac{\pi}{RT} = \frac{8.00 \text{ atm}}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 0.327 \text{ mol/L} \)

63. \( \Delta T_b = 77.85°C - 76.50°C = 1.35°C \); \( m = \frac{\Delta T_b}{K_b} = \frac{1.35°C}{5.03°C \text{ kg/mol}} = 0.268 \text{ mol/kg} \)

Mol biomolecule = 0.0150 kg solvent \times \frac{0.268 \text{ mol hydrocarbon}}{\text{kg solvent}} = 4.02 \times 10^{-3} \text{ mol}

From the problem, 2.00 g biomolecule was used, which must contain \( 4.02 \times 10^{-3} \text{ mol} \) biomolecule. The molar mass of the biomolecule is:

\[
\frac{2.00 \text{ g}}{4.02 \times 10^{-3} \text{ mol}} = 498 \text{ g/mol}
\]

64. \( M = \frac{\pi}{RT} = \frac{0.745 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300. \text{ K}} = 3.98 \times 10^{-5} \text{ mol/L} \)

\[
1.00 \text{ L} \times \frac{3.98 \times 10^{-5} \text{ mol}}{\text{L}} = 3.98 \times 10^{-5} \text{ mol catalase}
\]

Molar mass = \( \frac{10.00 \text{ g}}{3.98 \times 10^{-5} \text{ mol}} = 2.51 \times 10^5 \text{ g/mol} \)

65. \( \Delta T_f = K_f m, \ m = \frac{\Delta T_f}{K_f} = \frac{0.300°C}{5.12°C \text{ kg/mol}} = 5.86 \times 10^{-2} \text{ mol thryoxine} \text{ kg benzene} \)

The moles of thryoxine present are:

\[
0.0100 \text{ kg benzene} \times \frac{5.86 \times 10^{-2} \text{ mol thryoxine}}{\text{kg benzene}} = 5.86 \times 10^{-4} \text{ mol thryoxine}
\]
From the problem, 0.455 g thyroxine was used; this must contain $5.86 \times 10^{-4}$ mol thyroxine. The molar mass of the thyroxine is:

$$\text{molar mass} = \frac{0.455 \text{ g}}{5.86 \times 10^{-4} \text{ mol}} = 776 \text{ g/mol}$$

66. $m = \frac{\Delta T_f}{K_f} = \frac{30.0^\circ \text{C}}{1.86 \text{ } ^\circ \text{C} \text{ kg/mol}} = 16.1 \text{ mol C}_2\text{H}_6\text{O}_2/\text{kg}$

Because the density of water is 1.00 g/cm$^3$, the moles of C$_2$H$_6$O$_2$ needed are:

$$15.0 \text{ L H}_2\text{O} \times \frac{1.00 \text{ kg H}_2\text{O}}{\text{L H}_2\text{O}} \times \frac{16.1 \text{ mol C}_2\text{H}_6\text{O}_2}{\text{kg H}_2\text{O}} = 242 \text{ mol C}_2\text{H}_6\text{O}_2$$

Volume C$_2$H$_6$O$_2$ = 242 mol C$_2$H$_6$O$_2$ × $\frac{62.07 \text{ g}}{\text{mol C}_2\text{H}_6\text{O}_2} \times \frac{1 \text{ cm}^3}{1.11 \text{ g}} = 13,500 \text{ cm}^3 = 13.5 \text{ L}$

$$\Delta T_b = K_{b\text{m}} = \frac{0.51 ^\circ \text{C}}{\text{molal}} \times 16.1 \text{ molal} = 8.2 ^\circ \text{C}; \ T_b = 100.0^\circ \text{C} + 8.2^\circ \text{C} = 108.2^\circ \text{C}$$

67. $M = \frac{1.0 \text{ g}}{\text{L}} \times \frac{1 \text{ mol}}{9.0 \times 10^{-4} \text{ g}} = 1.1 \times 10^{-5} \text{ mol/ L}; \ \pi = MRT$

At 298 K: $\pi = \frac{1.1 \times 10^{-5} \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L atm}}{\text{K} \text{ mol}} \times 298 \text{ K} \times \frac{760 \text{ torr}}{\text{atm}}$, $\pi = 0.20 \text{ torr}$

Because d = 1.0 g/cm$^3$, 1.0 L of solution has a mass of 1.0 kg. Because only 1.0 g of protein is present per liter solution, 1.0 kg of H$_2$O is present, and molality equals molarity to the correct number of significant figures.

$$\Delta T_f = K_{f\text{m}} = \frac{1.86 ^\circ \text{C}}{\text{molal}} \times 1.1 \times 10^{-5} \text{ molal} = 2.0 \times 10^{-5} ^\circ \text{C}$$

68. Osmotic pressure is better for determining the molar mass of large molecules. A temperature change of $10^{-5} ^\circ \text{C}$ is very difficult to measure. A change in height of a column of mercury by 0.2 mm (0.2 torr) is not as hard to measure precisely.

69. $\pi = MRT = \frac{0.1 \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L atm}}{\text{K} \text{ mol}} \times 298 \text{ K} = 2.45 \text{ atm} \approx 2 \text{ atm}$

$$\pi = 2 \text{ atm} \times \frac{760 \text{ mm Hg}}{\text{atm}} \approx 2000 \text{ mm} \approx 2 \text{ m}$$

The osmotic pressure would support a mercury column of approximately 2 m. The height of a fluid column in a tree will be higher because Hg is more dense than the fluid in a tree. If we
assume the fluid in a tree is mostly H₂O, then the fluid has a density of 1.0 g/cm³. The density of Hg is 13.6 g/cm³.

Height of fluid \( \approx 2 \text{ m} \times 13.6 \approx 30 \text{ m} \)

70. \( \Delta T_f = 5.51 - 2.81 = 2.70^\circ\text{C} \); \( m = \frac{\Delta T_f}{K_f} = \frac{2.70^\circ\text{C}}{5.12 \text{ m}^2/\text{mol} \cdot \text{K}} = 0.527 \text{ molal} \)

Let \( x \) = mass of naphthalene (molar mass = 128.2 g/mol). Then \( 1.60 - x \) = mass of anthracene (molar mass = 178.2 g/mol).

\[
\frac{x}{128.2} = \text{moles naphthalene} \quad \text{and} \quad \frac{1.60 - x}{178.2} = \text{moles anthracene}
\]

\[
\frac{0.527 \text{ mol solute}}{\text{kg solvent}} = \frac{x}{128.2} + \frac{1.60 - x}{178.2}, \quad 1.05 \times 10^{-2} = \frac{(178.2)x + 1.60(128.2) - (128.2)x}{128.2(178.2)}
\]

\((50.0)x + 205 = 240, \quad (50.0)x = 240 - 205, \quad (50.0)x = 35, \quad x = 0.70 \text{ g naphthalene}\)

So the mixture is:

\[
\frac{0.70 \text{ g}}{1.60 \text{ g}} \times 100 = 44\% \text{ naphthalene by mass and 56\% anthracene by mass}
\]

71. With addition of salt or sugar, the osmotic pressure inside the fruit cells (and bacteria) is less than outside the cell. Water will leave the cells, which will dehydrate any bacteria present, causing them to die.

**Properties of Electrolyte Solutions**

72. A strong electrolyte dissociates completely into ions in solution. A weak electrolyte dissociates only partially into ions in solution. Colligative properties depend on the total number of particles in solution. By measuring a property such as freezing-point depression, boiling-point elevation, or osmotic pressure, we can calculate the van’t Hoff factor \( i \) to see if an electrolyte is strong or weak.

73. \( 19.6 \text{ torr} = \chi_{H_2O}(23.8 \text{ torr}), \quad \chi_{H_2O} = 0.824; \quad \chi_{\text{solute}} = 1.000 - 0.824 = 0.176 \)

0.176 is the mole fraction of all the solute particles present. Because NaCl dissociates to produce two ions in solution (Na⁺ and Cl⁻), 0.176 is the mole fraction of Na⁺ and Cl⁻ ions present. The mole fraction of NaCl is \( 1/2 \) (0.176) = 0.0880 = \( \chi_{\text{NaCl}} \).

At 45°C, \( P_{\text{solv}} = 0.824(71.9 \text{ torr}) = 59.2 \text{ torr} \).
74. If ideal, NaCl dissociates completely, and \( i = 2.0 \). \( \Delta T_f = iK_f m \); assuming water freezes at 0.00°C:

\[
1.28°C = 2 \times 1.86 °C \text{ kg/mol} \times m, \quad m = 0.344 \text{ mol NaCl/kg H}_2\text{O}
\]

Assume an amount of solution that contains 1.00 kg of water (solvent).

\[
0.344 \text{ mol NaCl} \times \frac{58.44 \text{ g}}{\text{mol}} = 20.1 \text{ g NaCl}
\]

Mass % NaCl = \[
\frac{20.1 \text{ g}}{1.00 \times 10^3 \text{ g} + 20.1 \text{ g}} \times 100 = 1.97%\]

75. \( \text{Na}_3\text{PO}_4(s) \rightarrow 3 \text{ Na}^+(aq) + \text{PO}_4^{3-}(aq), \ i = 4.0; \ \text{CaBr}_2(s) \rightarrow \text{Ca}^{2+}(aq) + 2 \text{ Br}^-(aq), \ i = 3.0 \)

\( \text{KCl}(s) \rightarrow \text{K}^+(aq) + \text{Cl}^-(aq), \ i = 2.0 \)

The effective particle concentrations of the solutions are (assuming complete dissociation):

\[
4.0(0.010 \text{ molal}) = 0.040 \text{ molal for the Na}_3\text{PO}_4 \text{ solution}; \ 3.0(0.020 \text{ molal}) = 0.060 \text{ molal for the CaBr}_2 \text{ solution}; \ 2.0(0.020 \text{ molal}) = 0.040 \text{ molal for the KCl solution}; \ \text{slightly greater than 0.020 molal for the HF solution because HF only partially dissociates in water (it is a weak acid).}
\]

a. The 0.010 \text{ m Na}_3\text{PO}_4 \text{ solution and the 0.020 m KCl solution both have effective particle concentrations of 0.040 m (assuming complete dissociation), so both of these solutions should have the same boiling point as the 0.040 m C}_6\text{H}_12\text{O}_6 \text{ solution (a nonelectrolyte).}

b. \( P = \chi P^0 \); as the solute concentration decreases, the solvent’s vapor pressure increases because \( \chi \) increases. Therefore, the 0.020 \text{ m HF solution will have the highest vapor pressure because it has the smallest effective particle concentration.}

c. \( \Delta T = K_f m \); the 0.020 \text{ m CaBr}_2 \text{ solution has the largest effective particle concentration, so it will have the largest freezing point depression (largest } \Delta T).\)

76. The solutions of glucose, NaCl and CaCl\(_2\) will all have lower freezing points, higher boiling points, and higher osmotic pressures than pure water. The solution with the largest particle concentration will have the lowest freezing point, the highest boiling point, and the highest osmotic pressure. The CaCl\(_2\) solution will have the largest effective particle concentration because it produces three ions per mole of compound.

a. pure water  

b. CaCl\(_2\) solution  

c. CaCl\(_2\) solution

d. pure water  

e. CaCl\(_2\) solution

77. The van’t Hoff factor \( i \) is the number of moles of particles (ions) produced for every mole of solute dissolved. For NaCl, \( i = 2 \) since Na\(^+\) and Cl\(^-\) are produced in water; for Al(NO\(_3\))\(_3\), \( i = 4 \) since Al\(^3+\) and 3 NO\(_3^-\) ions are produced when Al(NO\(_3\))\(_3\) dissolves in water. In real life, the van’t Hoff factor is rarely the value predicted by the number of ions a salt dissolves into; \( i \) is
generally something less than the predicted number of ions. This is due to a phenomenon called ion pairing, where at any instant a small percentage of oppositely charged ions pair up and act like a single solute particle. Ion pairing occurs most when the concentration of ions is large. Therefore, dilute solutions behave most ideally; here, i is close to that determined by the number of ions in a salt.

78. a. As discussed in Figure 17.16 of the text, the water would migrate from right to left. Initially, the level of liquid in the right arm would go down, and the level in the left arm would go up. At some point the rate of solvent transfer will be the same in both directions, and the levels of the liquids in the two arms will stabilize. The height difference between the two arms will be a measure of the osmotic pressure of the NaCl solution.

b. Initially, H₂O molecules will have a net migration into the NaCl side. However, NaCl molecules can now migrate into the H₂O side. Because solute and solvent transfer are both possible, the levels of the liquids will be equal once the rate of solute and solvent transfer is equal in both directions. At this point the concentration of NaCl will be equal in both chambers, and the levels of liquid will be equal.

79. \( \text{NaCl(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-\text{(aq)}, \ i = 2.0 \)

\[ \pi = iMRT = 2.0 \times \frac{0.10 \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L atm}}{\text{K mol}} \times 293 \text{ K} = 4.8 \text{ atm} \]

A pressure greater than 4.8 atm should be applied to ensure purification by reverse osmosis.

80. a. \( \text{MgCl}_2\text{(s)} \rightarrow \text{Mg}^{2+}(\text{aq}) + 2 \text{Cl}^-\text{(aq)}, \ i = 3.0 \text{ mol ions/mol solute} \)

\[ \Delta T_f = iK_f m = 3.0 \times 1.86 \degree \text{C/molal} \times 0.050 \text{ molal} = 0.28 \degree \text{C}; \ T_f = -0.28 \degree \text{C} \ (\text{Assuming water freezes at 0.00} \degree \text{C.}) \]

\[ \Delta T_b = iK_b m = 3.0 \times 0.51 \degree \text{C/molal} \times 0.050 \text{ molal} = 0.077 \degree \text{C}; \ T_b = 100.077 \degree \text{C} \ (\text{Assuming water boils at 100.000} \degree \text{C.}) \]

b. \( \text{FeCl}_3\text{(s)} \rightarrow \text{Fe}^{3+}(\text{aq}) + 3 \text{Cl}^-\text{(aq)}, \ i = 4.0 \text{ mol ions/mol solute} \)

\[ \Delta T_f = iK_f m = 4.0 \times 1.86 \degree \text{C/molal} \times 0.050 \text{ molal} = 0.37 \degree \text{C}; \ T_f = -0.37 \degree \text{C} \]

\[ \Delta T_b = iK_b m = 4.0 \times 0.51 \degree \text{C/molal} \times 0.050 \text{ molal} = 0.10 \degree \text{C}; \ T_b = 100.10 \degree \text{C} \]

81. a. \( \text{MgCl}_2, \ i \text{ (observed)} = 2.7 \)

\[ \Delta T_f = iK_f m = 2.7 \times 1.86 \degree \text{C/molal} \times 0.050 \text{ molal} = 0.25 \degree \text{C}; \ T_f = -0.25 \degree \text{C} \]

\[ \Delta T_b = iK_b m = 2.7 \times 0.51 \degree \text{C/molal} \times 0.050 \text{ molal} = 0.069 \degree \text{C}; \ T_b = 100.069 \degree \text{C} \]

b. \( \text{FeCl}_3, \ i \text{ (observed)} = 3.4 \)

\[ \Delta T_f = iK_f m = 3.4 \times 1.86 \degree \text{C/molal} \times 0.050 \text{ molal} = 0.32 \degree \text{C}; \ T_f = -0.32 \degree \text{C} \]

\[ \Delta T_b = iK_b m = 3.4 \times 0.51 \degree \text{C/molal} \times 0.050 \text{ molal} = 0.087 \degree \text{C}; \ T_b = 100.087 \degree \text{C} \]
82. \[ \Delta T_f = i K_f m, \quad i = \frac{\Delta T_f}{K_f m} \]

For 0.0225 molal CaCl₂,

\[ i = \frac{0.440}{1.86 \times 0.0910} = 2.60 \text{ for } 0.0910 \text{ mol CaCl}_2 \]

\[ i = \frac{1.330}{1.86 \times 0.278} = 2.57 \text{ for } 0.278 \text{ mol CaCl}_2 \]

Note that i is less than the ideal value of 3.0 for CaCl₂. This is due to ion pairing in solution.

83. \[ \pi = i MRT \]

\[ M = \frac{\pi}{i R T} \]

\[ \pi = \frac{2.50 \text{ atm}}{2.00 \times 0.08206 \text{ L atm K mol}^{-1}} 	imes 298 \text{ K} = 5.11 \times 10^{-2} \text{ mol/L} \]

Molar mass of compound = \[ \frac{0.500 \text{ g}}{0.1000 \text{ L} \times 5.11 \times 10^{-2} \text{ mol/L}} = 97.8 \text{ g/mol} \]

84. a. \[ T_c = 5(T_f - 32)/9 = 5(-29 - 32)/9 = -34^\circ C \]

Assuming the solubility of CaCl₂ is temperature independent, the molality of a saturated CaCl₂ solution is:

\[ \frac{74.5 \text{ g CaCl}_2}{100.0 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g}}{110.98 \text{ g CaCl}_2} = 6.71 \text{ mol CaCl}_2/\text{kg H}_2\text{O} \]

\[ \Delta T_f = i K_f m = 3.00 \times 1.86 \text{ °C kg/mol} \times 6.71 \text{ mol/kg} = 37.4^\circ C \]

Assuming i = 3.00, a saturated solution of CaCl₂ can lower the freezing point of water to \(-37.4^\circ C\). Assuming these conditions, a saturated CaCl₂ solution should melt ice at \(-34^\circ C\) \((-29^\circ F\)).

b. From Exercise 17.82, i \approx 2.6; \[ \Delta T_f = i K_f m = 2.6 \times 1.86 \times 6.71 = 32^\circ C; \quad T_f = -32^\circ C. \]

Assuming i = 2.6, a saturated CaCl₂ solution will not melt ice at \(-34^\circ C\) \((-29^\circ F\)).

Additional Exercises

85. Both solutions and colloids have suspended particles in some medium. The major difference between the two is the size of the particles. A colloid is a suspension of relatively large particles compared to a solution. Because of this, colloids will scatter light, whereas solutions will not. The scattering of light by a colloidal suspension is called the Tyndall effect.

86. The micelles form so that the ionic ends of the detergent molecules, the SO₄⁻ ends, are exposed to the polar water molecules on the outside, whereas the nonpolar hydrocarbon chains from the detergent molecules are hidden from the water by pointing toward the inside of the micelle. Dirt, which is basically nonpolar, is stabilized in the nonpolar interior of the micelle and is washed away.
87. Coagulation is the destruction of a colloid by the aggregation of many suspended particles to form a large particle that settles out of solution.

88. The main factor for stabilization seems to be electrostatic repulsion. The center of a colloid particle is surrounded by a layer of same charged ions, with oppositely charged ions forming another charged layer on the outside. Overall, there are equal numbers of charged and oppositely charged ions, so the colloidal particles are electrically neutral. However, since the outer layers are the same charge, the particles repel each other and do not easily aggregate for precipitation to occur.

Heating increases the velocities of the colloidal particles. This causes the particles to collide with enough energy to break the ion barriers, allowing the colloids to aggregate and eventually precipitate out. Adding an electrolyte neutralizes the adsorbed ion layers, which allows colloidal particles to aggregate and then precipitate out.

89. A 92 proof ethanol solution is 46% C₂H₅OH by volume. Assuming 100.0 mL of solution:

\[
\text{mol ethanol} = 46 \text{ mL C}_2\text{H}_5\text{OH} \times \frac{0.79 \text{ g}}{\text{mL}} \times \frac{1 \text{ mol C}_2\text{H}_5\text{OH}}{46.07 \text{ g}} = 0.79 \text{ mol C}_2\text{H}_5\text{OH}
\]

\[
\text{molarity} = \frac{0.79 \text{ mol}}{0.1000 \text{ L}} = 7.9 \text{ M ethanol}
\]

90. Mass of H₂O = 160. mL \times \frac{0.995 \text{ g}}{\text{mL}} = 159 \text{ g} = 0.159 \text{ kg}

\[
\text{Mol NaDTZ} = 0.159 \text{ kg} \times \frac{0.378 \text{ mol}}{\text{kg}} = 0.0601 \text{ mol}
\]

\[
\text{Molar mass of NaDTZ} = \frac{38.4 \text{ g}}{0.0601 \text{ mol}} = 639 \text{ g/mol}
\]
\[
\text{Psoln} = \chi_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}^\circ; \quad \text{mol H}_2\text{O} = 159 \, \text{g} \times \frac{1 \, \text{mol}}{18.02 \, \text{g}} = 8.82 \, \text{mol}
\]

Sodium diatrizoate is a salt because there is a metal (sodium) in the compound. From the short-hand notation for sodium diatrizoate, NaDTZ, we can assume this salt breaks up into Na\(^+\) and DTZ\(^-\) ions. So the moles of solute particles are \(2(0.0601) = 0.120 \, \text{mol solute particles}\).

\[
\chi_{\text{H}_2\text{O}} = \frac{8.82 \, \text{mol}}{0.120 \, \text{mol} + 8.82 \, \text{mol}} = 0.987; \quad \text{Psoln} = 0.987 \times 34.1 \, \text{torr} = 33.7 \, \text{torr}
\]

91. \(\Delta T = K_f m, \quad m = \frac{\Delta T}{K_f} = \frac{2.79^\circ \text{C}}{1.86 \, \text{^\circ C/molal}} = 1.50 \, \text{molal}\)

a. \(\Delta T = K_b m, \quad \Delta T = (0.51 \, \text{^\circ C/molal})(1.50 \, \text{molal}) = 0.77^\circ \text{C}, \quad T_b = 100.77^\circ \text{C}\)

b. \(\text{Psoln} = \chi_{\text{water}} P_{\text{water}}^\circ \chi_{\text{water}} = \frac{\text{mol H}_2\text{O}}{\text{mol H}_2\text{O} + \text{mol solute}}\)

Assuming 1.00 kg of water, we have 1.50 mol solute, and:

\[
\text{mol H}_2\text{O} = 1.00 \times 10^3 \, \text{g H}_2\text{O} \times \frac{1 \, \text{mol H}_2\text{O}}{18.02 \, \text{g H}_2\text{O}} = 55.5 \, \text{mol H}_2\text{O}
\]

\[
\chi_{\text{water}} = \frac{55.5 \, \text{mol}}{1.50 + 55.5} = 0.974; \quad \text{Psoln} = (0.974)(23.76 \, \text{mm Hg}) = 23.1 \, \text{mm Hg}
\]

c. We assumed ideal behavior in solution formation, we assumed the solute was nonvolatile, and we assumed \(i = 1\) (no ions formed).

92. \(\Delta T = i m K_f, \quad i = \frac{\Delta T}{m K_f} = \frac{2.79^\circ \text{C}}{0.250 \, \text{mol} \times \frac{1.86 \, \text{^\circ C kg}}{0.500 \, \text{kg mol}}} = 3.00\)

We have three ions in solutions, and we have twice as many anions as cations. Therefore, the formula of Q is MCl\(_2\). Assuming 100.00 g of compound:

\[
38.68 \, \text{g Cl} \times \frac{1 \, \text{mol Cl}}{35.45 \, \text{g}} = 1.091 \, \text{mol Cl}
\]

\[
\text{mol M} = 1.091 \, \text{mol Cl} \times \frac{1 \, \text{mol M}}{2 \, \text{mol Cl}} = 0.5455 \, \text{mol M}
\]

Molar mass of M = \(\frac{61.32 \, \text{g M}}{0.5455 \, \text{mol M}} = 112.4 \, \text{g/mol}; \quad \text{M is Cd, so Q = CdCl}_2\).
93. Benzoic acid is capable of hydrogen-bonding, but a significant part of benzoic acid is the nonpolar benzene ring. In benzene, a hydrogen-bonded dimer forms.

[Diagram of a hydrogen-bonded dimer]

The dimer is relatively nonpolar and thus more soluble in benzene than in water. Because benzoic acid forms dimers in benzene, the effective solute particle concentration will be less than 1.0 molal. Therefore, the freezing-point depression would be less than \(5.12^\circ C\) (\(\Delta T_f = K_f m\)).

94. Benzoic acid (see Exercise 93) would be more soluble in a basic solution because of the reaction:

\[
C_6H_5CO_2H + OH^- \rightarrow C_6H_5CO_2^- + H_2O
\]

By removing the proton from benzoic acid, an anion forms, and like all anions, the species becomes more soluble in water.

95. a. \(\text{NH}_4\text{NO}_3(s) \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq)\) \(\Delta H_{\text{soln}} = ?\)

Heat gain by dissolution process = heat loss by solution; We will keep all quantities positive in order to avoid sign errors. Because the temperature of the water decreased, the dissolution of \(\text{NH}_4\text{NO}_3\) is endothermic (\(\Delta H\) is positive). Mass of solution = 1.60 + 75.0 = 76.6 g

Heat loss by solution \(= \frac{4.18 \text{J}}{\text{g} \cdot ^\circ C} \times 76.6 \text{g} \times (25.00^\circ C - 23.34^\circ C) = 532 \text{J}

\[
\Delta H_{\text{soln}} = \frac{532 \text{J}}{1.60 \text{g} \text{NH}_4\text{NO}_3} \times \frac{80.05 \text{g} \text{NH}_4\text{NO}_3}{\text{mol} \text{NH}_4\text{NO}_3} = 2.66 \times 10^4 \text{J/mol} = 26.6 \text{kJ/mol}
\]

b. We will use Hess’s law to solve for the lattice energy. The lattice energy equation is:

\[
\text{NH}_4^+(g) + \text{NO}_3^-(g) \rightarrow \text{NH}_4\text{NO}_3(s) \quad \Delta H = \text{lattice energy}
\]

\[
\text{NH}_4^+(g) + \text{NO}_3^-(g) \rightarrow \text{NH}_4^+(aq) + \text{NO}_3^-(aq) \quad \Delta H = \Delta H_{\text{hyd}} = -630. \text{kJ/mol}
\]

\[
\text{NH}_4^+(aq) + \text{NO}_3^-(aq) \rightarrow \text{NH}_4\text{NO}_3(s) \quad \Delta H = -\Delta H_{\text{soln}} = -26.6 \text{kJ/mol}
\]

\[
\text{NH}_4^+(g) + \text{NO}_3^-(g) \rightarrow \text{NH}_4\text{NO}_3(s) \quad \Delta H = \Delta H_{\text{hyd}} - \Delta H_{\text{soln}} = -657 \text{kJ/mol}
\]
96. a. The average values for each ion are:

\[ 300. \text{ mg Na}^+, \ 15.7 \text{ mg K}^+, \ 5.45 \text{ mg Ca}^{2+}, \ 388 \text{ mg Cl}^-, \ \text{and 246 mg lactate (C}_3\text{H}_5\text{O}_3^-) \]

Note: Because we can precisely weigh to ±0.1 mg on an analytical balance, we'll carry extra significant figures and calculate results to ±0.1 mg.

The only source of lactate is NaC\textsubscript{3}H\textsubscript{5}O\textsubscript{3}.

\[
246 \text{ mg C}_3\text{H}_5\text{O}_3^- \times \frac{112.06 \text{ mg NaC}_3\text{H}_5\text{O}_3^-}{89.07 \text{ mg C}_3\text{H}_5\text{O}_3^-} = 309.5 \text{ mg sodium lactate}
\]

The only source of Ca\textsuperscript{2+} is CaCl\textsubscript{2} • 2H\textsubscript{2}O.

\[
5.45 \text{ mg Ca}^{2+} \times \frac{147.0 \text{ mg CaCl}_2 \cdot 2\text{H}_2\text{O}}{40.08 \text{ mg Ca}^{2+}} = 19.99 \text{ or 20.0 mg CaCl}_2 \cdot 2\text{H}_2\text{O}
\]

The only source of K\textsuperscript{+} is KCl.

\[
15.7 \text{ mg K}^+ \times \frac{74.55 \text{ mg KCl}}{39.10 \text{ mg K}^+} = 29.9 \text{ mg KCl}
\]

From what we have used already, let's calculate the mass of Na\textsuperscript{+} added.

\[
309.5 \text{ mg sodium lactate} - 246.0 \text{ mg lactate} = 63.5 \text{ mg Na}^+
\]

Thus we need to add an additional 236.5 mg Na\textsuperscript{+} to get the desired 300. mg.

\[
236.5 \text{ mg Na}^+ \times \frac{58.44 \text{ mg NaCl}}{22.99 \text{ mg Na}^+} = 601.2 \text{ mg NaCl}
\]

Now let's check the mass of Cl\textsuperscript{-} added:

\[
20.0 \text{ mg CaCl}_2 \cdot 2\text{H}_2\text{O} \times \frac{70.90 \text{ mg Cl}^-}{147.0 \text{ mg CaCl}_2 \cdot 2\text{H}_2\text{O}} = 9.6 \text{ mg Cl}^-
\]

\[
20.0 \text{ mg CaCl}_2 \cdot 2\text{H}_2\text{O} = 9.6 \text{ mg Cl}^-
\]

\[
29.9 \text{ mg KCl} - 15.7 \text{ mg K}^+ = 14.2 \text{ mg Cl}^-
\]

\[
601.2 \text{ mg NaCl} - 236.5 \text{ mg Na}^+ = 364.7 \text{ mg Cl}^-
\]

\[
\text{Total Cl}^- = 388.5 \text{ mg Cl}^-
\]

This is the quantity of Cl\textsuperscript{-} we want (the average amount of Cl\textsuperscript{-}).

An analytical balance can weigh to the nearest 0.1 mg. We would use 309.5 mg sodium lactate, 20.0 mg CaCl\textsubscript{2} • 2H\textsubscript{2}O, 29.9 mg KCl, and 601.2 mg NaCl.
b. To get the range of osmotic pressure, we need to calculate the molar concentration of each ion at its minimum and maximum values. At minimum concentrations, we have:

\[
\begin{align*}
\text{Na}^+ & \quad \frac{285 \text{ mg}}{100 \text{ mL}} \times \frac{1 \text{ mmol}}{22.99 \text{ mg}} = 0.124 \text{ M}; \\
\text{K}^+ & \quad \frac{14.1 \text{ mg}}{100 \text{ mL}} \times \frac{1 \text{ mmol}}{39.10 \text{ mg}} = 0.00361 \text{ M} \\
\text{Ca}^{2+} & \quad \frac{4.9 \text{ mg}}{100 \text{ mL}} \times \frac{1 \text{ mmol}}{40.08 \text{ mg}} = 0.0012 \text{ M}; \\
\text{Cl}^- & \quad \frac{368 \text{ mg}}{100 \text{ mL}} \times \frac{1 \text{ mmol}}{35.45 \text{ mg}} = 0.104 \text{ M} \\
\text{C}_3\text{H}_5\text{O}_3^- & \quad \frac{231 \text{ mg}}{100 \text{ mL}} \times \frac{1 \text{ mmol}}{89.07 \text{ mg}} = 0.0259 \text{ M} \\
\end{align*}
\]

Total = 0.124 + 0.00361 + 0.0012 + 0.104 + 0.0259 = 0.259 M

\[
\pi = MRT = \frac{0.259 \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L atm}}{\text{mol K}} \times 310. \text{ K} = 6.59 \text{ atm}
\]

Similarly, at maximum concentrations, the concentration for each ion is:

\[
\begin{align*}
\text{Na}^+ & \quad 0.137 \text{ M}; \\
\text{K}^+ & \quad 0.00442 \text{ M}; \\
\text{Ca}^{2+} & \quad 0.0015 \text{ M}; \\
\text{Cl}^- & \quad 0.115 \text{ M}; \\
\text{C}_3\text{H}_5\text{O}_3^- & \quad 0.0293 \text{ M}
\end{align*}
\]

The total concentration of all ions is 0.287 M.

\[
\pi = \frac{0.287 \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L atm}}{\text{K mol}} \times 310. \text{ K} = 7.30 \text{ atm}
\]

Osmotic pressure ranges from 6.59 atm to 7.30 atm.

97. \(\chi_{\text{pen}}^{V} = 0.15 = \frac{P_{\text{pen}}}{P_{\text{total}}}; \quad P_{\text{pen}} = \chi_{\text{pen}}^{L} P_{\text{pen}}^{0}; \quad P_{\text{total}} = P_{\text{pen}} + P_{\text{hex}} = \chi_{\text{pen}}^{L}(511) + \chi_{\text{hex}}^{L}(150).\)

Because \(\chi_{\text{hex}}^{L} = 1.00 - \chi_{\text{pen}}^{L}; \quad P_{\text{total}} = \chi_{\text{pen}}^{L}(511) + (1.00 - \chi_{\text{pen}}^{L})(150.) = 150. + 361 \chi_{\text{pen}}^{L}\)

\[
\chi_{\text{pen}}^{V} = \frac{P_{\text{pen}}}{P_{\text{total}}}, \quad 0.15 = \frac{\chi_{\text{pen}}^{L}(511)}{150. + 361 \chi_{\text{pen}}^{L}}, \quad 0.15(150. + 361 \chi_{\text{pen}}^{L}) = 511 \chi_{\text{pen}}^{L}
\]

\[
23 + 54 \chi_{\text{pen}}^{L} = 511 \chi_{\text{pen}}^{L}, \quad \chi_{\text{pen}}^{L} = \frac{23}{457} = 0.050
\]

98. a. Water boils when the vapor pressure equals the pressure above the water. In an open pan, \(P_{\text{atm}} \approx 1.0 \text{ atm}.\) In a pressure cooker, \(P_{\text{inside}} > 1.0 \text{ atm},\) and water boils at a higher temperature. The higher the cooking temperature, the faster is the cooking time.

b. Salt dissolves in water, forming a solution with a melting point lower than that of pure water (\(\Delta T_f = K_f m).\) This happens in water on the surface of ice. If it is not too cold, the ice melts. This won't work if the ambient temperature is lower than the depressed freezing point of the salt solution.
c. When water freezes from a solution, it freezes as pure water, leaving behind a more concentrated salt solution.

d. On the CO₂ phase diagram, the triple point is above 1 atm, and CO₂(g) is the stable phase at 1 atm and room temperature. CO₂(l) can’t exist at normal atmospheric pressures. Therefore, dry ice sublimes instead of boils. In a fire extinguisher, P > 1 atm and CO₂(l) can exist. When CO₂ is released from the fire extinguisher, CO₂(g) forms as predicted from the phase diagram.

99. \[ 14.2 \text{ mg CO}_2 \times \frac{12.01 \text{ mg C}}{44.01 \text{ mg CO}_2} = 3.88 \text{ mg C}; \quad \% \text{ C} = \frac{3.88 \text{ mg}}{4.80 \text{ mg}} \times 100 = 80.8\% \text{ C} \]

\[ 1.65 \text{ mg H}_2\text{O} \times \frac{2.016 \text{ mg H}}{18.02 \text{ mg H}_2\text{O}} = 0.185 \text{ mg H}; \quad \% \text{ H} = \frac{0.185 \text{ mg}}{4.80 \text{ mg}} \times 100 = 3.85\% \text{ H} \]

Mass \% O = 100.00 – (80.8 + 3.85) = 15.4\% O

Out of 100.00 g:

\[ 80.8 \text{ g C} \times \frac{1 \text{ mol}}{12.01 \text{ g}} = 6.73 \text{ mol C}; \quad \frac{6.73}{0.963} = 6.99 \approx 7 \]

\[ 3.85 \text{ g H} \times \frac{1 \text{ mol}}{1.008 \text{ g}} = 3.82 \text{ mol H}; \quad \frac{3.82}{0.963} = 3.97 \approx 4 \]

\[ 15.4 \text{ g O} \times \frac{1 \text{ mol}}{16.00 \text{ g}} = 0.963 \text{ mol O}; \quad \frac{0.963}{0.963} = 1.00 \]

Therefore, the empirical formula is \text{C}_7\text{H}_4\text{O}.

\[ \Delta T_f = K_f m, \quad m = \frac{\Delta T_f}{K_f} = \frac{22.3 ^\circ C}{40. ^\circ C / \text{ molal}} = 0.56 \text{ molal} \]

\[ \text{Mol anthraquinone} = 0.0114 \text{ kg camphor} \times \frac{0.56 \text{ mol anthraquinone}}{\text{kg camphor}} = 6.4 \times 10^{-3} \text{ mol} \]

\[ \text{Molar mass} = \frac{1.32 \text{ g}}{6.4 \times 10^{-3} \text{ mol}} = 210 \text{ g/mol} \]

The empirical mass of \text{C}_7\text{H}_4\text{O} is 7(12) + 4(1) + 16 \approx 104 \text{ g/mol}. Because the molar mass is twice the empirical mass, the molecular formula is \text{C}_{14}\text{H}_8\text{O}_2.

100. Out of 100.00 g, there are:

\[ 31.57 \text{ g C} \times \frac{1 \text{ mol C}}{12.011 \text{ g}} = 2.628 \text{ mol C}; \quad \frac{2.628}{2.628} = 1.000 \]
5.30 g H × \frac{1 \text{ mol H}}{1.008 \text{ g}} = 5.26 \text{ mol H; } \frac{5.26}{2.628} = 2.00

63.13 g O \times \frac{1 \text{ mol O}}{15.999 \text{ g}} = 3.946 \text{ mol O; } \frac{3.946}{2.628} = 1.502

Empirical formula: C_2H_4O_3; use the freezing-point data to determine the molar mass.

\[ m = \frac{\Delta T_f}{K_f} = \frac{5.20°C}{1.86°C/\text{molal}} = 2.80 \text{ molal} \]

Mol solute = 0.0250 kg × \frac{2.80 \text{ mol solute}}{\text{kg}} = 0.0700 \text{ mol solute}

Molar mass = \frac{10.56 \text{ g}}{0.0700 \text{ mol}} = 151 \text{ g/mol}

The empirical formula mass of C_2H_4O_3 = 76.051 \text{ g/mol}. Because the molar mass is about twice the empirical mass, the molecular formula is C_4H_8O_6, which has a molar mass of 152.101 \text{ g/mol}.

Note: We use the experimental molar mass to determine the molecular formula. Knowing this, we calculate the molar mass precisely from the molecular formula using atomic masses.

101. a. \[ m = \frac{\Delta T_f}{K_f} = \frac{1.32°C}{5.12°C \text{ kg/mol}} = 0.258 \text{ mol/kg} \]

Mol unknown = 0.01560 kg × \frac{0.258 \text{ mol unknown}}{\text{kg}} = 4.02 × 10^{-3} \text{ mol}

Molar mass of unknown = \frac{1.22 \text{ g}}{4.02 × 10^{-3} \text{ mol}} = 303 \text{ g/mol}

Uncertainty in temperature = \frac{0.04}{1.32} × 100 = 3%

A 3% uncertainty in 303 g/mol = 9 g/mol.

So molar mass = 303 ±9 g/mol.

b. No, codeine could not be eliminated since its molar mass is in the possible range including the uncertainty.

c. We would like the uncertainty to be ±1 g/mol. We need the freezing-point depression to be about 10 times what it was in this problem. Two possibilities are:
CHAPTER 17  PROPERTIES OF SOLUTIONS

1. make the solution 10 times more concentrated (may be solubility problem)

2. use a solvent with a larger \( K_f \) value, e.g., camphor

102. \( MX \rightleftharpoons M^+ + X^- \) \( K_{sp} = [M^+][X^-] \); \( \Delta T = K_f m, \ m = \frac{\Delta T}{K_f} = \frac{0.028}{1.86} = 0.015 \) mol/kg

\[
\frac{0.015 \text{ mol}}{\text{kg}} \times \frac{1 \text{ kg}}{1000 \text{ g}} \times 250 \text{ g} = 0.00375 \text{ mol total solute particles (carrying extra sig. fig.)}
\]

Assume a solution density of 1.0 g/mL so that volume of solution = 250 mL.

\[
[M^+] = \frac{(0.00375/2)}{0.25 \text{ L}} = 7.5 \times 10^{-3} \text{ M}, \ [X^-] = \frac{(0.00375/2)}{0.25 \text{ L}} = 7.5 \times 10^{-3} \text{ M}
\]

\( K_{sp} = [M^+][X^-] = (7.5 \times 10^{-3})(7.5 \times 10^{-3}) = 5.6 \times 10^{-5} \)

103. \( M_3X_2(s) \rightarrow 3 M^{2+}(aq) + 2 X^{3-}(aq) \) \( K_{sp} = [M^{2+}]^3[X^{3-}]^2 \)

<table>
<thead>
<tr>
<th>Initial</th>
<th>( s ) = solubility (mol/L)</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equil.</td>
<td>( 3s )</td>
<td>2s</td>
<td>2s</td>
</tr>
</tbody>
</table>

\( K_{sp} = (3s)^3(2s)^2 = 108s^5 \); total ion concentration = \( 3s + 2s = 5s \).

\[
\pi = iMRT, \ iM = \text{total ion concentration} = \frac{\pi}{RT} = \frac{2.64 \times 10^{-2} \text{ atm}}{0.08206 \ L \ \text{atm} \ \text{K}^{-1} \ \text{mol}^{-1} \times 298 \text{ K}} = 1.08 \times 10^{-3} \text{ mol/L}
\]

\( 5s = 1.08 \times 10^{-3} \text{ mol/L}, \ s = 2.16 \times 10^{-4} \text{ mol/L} \)

\( K_{sp} = 108s^5 = 108(2.16 \times 10^{-4})^5 = 5.08 \times 10^{-17} \)

104. \( m = \frac{\Delta T_f}{K_f} = \frac{0.426 \degree C}{1.86 \degree C/\text{molal}} = 0.229 \text{ molal} \)

Assuming a solution density = 1.00 g/mL, then 1.00 L contains 0.229 mol solute.

\( \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \) \( i = 2; \) so: \( 2(\text{mol NaCl}) + \text{mol C}_{12}\text{H}_{22}\text{O}_{11} = 0.229 \text{ mol} \)

Mass \( \text{NaCl} + \text{mass C}_{12}\text{H}_{22}\text{O}_{11} = 20.0 \text{ g} \)

\( 2n_{\text{NaCl}} + n_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} = 0.229 \) and \( 58.44(n_{\text{NaCl}}) + 342.33(n_{\text{C}_{12}\text{H}_{22}\text{O}_{11}}) = 20.0 \)

Solving: \( n_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} = 0.0425 \text{ mol} = 14.5 \text{ g} \) and \( n_{\text{NaCl}} = 0.0932 \text{ mol} = 5.45 \text{ g} \)
Mass % C\textsubscript{12}H\textsubscript{22}O\textsubscript{11} = \frac{14.5 \text{ g}}{20.0 \text{ g} \times 100} = 72.5\% \text{ and 27.5}\% \text{ NaCl by mass}

\chi_{\text{C}_{12}\text{H}_{22}\text{O}_{11}} = \frac{0.0425 \text{ mol}}{0.0425 \text{ mol} + 0.0932 \text{ mol}} = 0.313

105. \quad m = \frac{0.100 \text{ g} \times \frac{1 \text{ mol}}{100.0 \text{ g}}}{0.5000 \text{ kg}} = 2.00 \times 10^{-3} \text{ mol/kg} \approx 2.00 \times 10^{-3} \text{ mol/L} \quad \text{(dilute solution)}

\Delta T_f = i K_f m, \quad 0.0056 \degree C = i(1.86 \degree C/molal)(2.00 \times 10^{-3} \text{ molal}), \quad i = 1.5

If i = 1.0, percent dissociation = 0%, and if i = 2.0, percent dissociation = 100%. Because i = 1.5, the weak acid is 50% dissociated.

HA \rightleftharpoons H^+ + A^- \quad K_a = \frac{[H^+][A^-]}{[HA]}

Because the weak acid is 50% dissociated:

\begin{align*}
[H^+] = [A^-] &= [HA]_0 \times 0.50 = 2.00 \times 10^{-3} M \times 0.50 = 1.0 \times 10^{-3} M \\
[HA] &= [HA]_0 - \text{amount HA reacted} = 2.00 \times 10^{-3} M - 1.0 \times 10^{-3} M = 1.0 \times 10^{-3} M
\end{align*}

\begin{align*}
K_a &= \frac{[H^+][A^-]}{[HA]} = \frac{(1.0 \times 10^{-3})(1.0 \times 10^{-3})}{1.0 \times 10^{-3}} = 1.0 \times 10^{-3}
\end{align*}

106. \quad \Delta T_f = K_f m, \quad m = \frac{\Delta T_f}{K_f} = \frac{5.40 \degree C}{1.86 \degree C/molal} = 2.90 \text{ molal}

\begin{align*}
\frac{2.90 \text{ mol solute}}{\text{kg solvent}} &= \frac{n}{0.0500 \text{ kg}}, \quad n = 0.145 \text{ mol of ions in solution}
\end{align*}

Because NaNO\textsubscript{3} and Mg(NO\textsubscript{3})\textsubscript{2} are strong electrolytes:

\begin{align*}
\quad n &= 2(x \text{ mol of NaNO}_3) + 3[y \text{ mol Mg(NO}_3)_2] = 0.145 \text{ mol ions}
\end{align*}

In addition: 6.50 g = x mol NaNO\textsubscript{3} \left(\frac{85.00 \text{ g}}{\text{mol}}\right) + y mol Mg(NO\textsubscript{3})\textsubscript{2} \left(\frac{148.3 \text{ g}}{\text{mol}}\right)

We have two equations: 2x + 3y = 0.145 \quad \text{and} \quad (85.00)x + (148.3)y = 6.50

Solving by simultaneous equations:
\[-(85.00)x - (127.5)y = -6.16\]
\[(85.00)x + (148.3)y = 6.50\]

\[(20.8)y = 0.34, \quad y = 0.016 \text{ mol Mg(NO}_3\text{)}_2\]

Mass of Mg(NO\(_3\))\(_2\) = 0.016 mol \times 148.3 g/mol = 2.4 g Mg(NO\(_3\))\(_2\), or 37% Mg(NO\(_3\))\(_2\) by mass

Mass of NaNO\(_3\) = 6.50 g - 2.4 g = 4.1 g NaNO\(_3\), or 63% NaNO\(_3\) by mass

107. 

\[iM = \frac{\pi}{RT} = \frac{0.3950 \text{ atm}}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}(298.2 \text{ K})} = 0.01614 \text{ mol/L} = \text{total ion concentration}\]

0.01614 mol/L = \(M_{\text{Mg}^{2+}} + M_{\text{Na}^+} + M_{\text{Cl}^-}\); \(M_{\text{Cl}^-} = 2M_{\text{Mg}^{2+}} + M_{\text{Na}^+}\) (charge balance)

Combining: \(0.01614 = 3M_{\text{Mg}^{2+}} + 2M_{\text{Na}^+}\)

Let \(x = \text{mass MgCl}_2\) and \(y = \text{mass NaCl}\); then \(x + y = 0.5000 \text{ g}\).

\[M_{\text{Mg}^{2+}} = \frac{x}{95.218} \quad \text{and} \quad M_{\text{Na}^+} = \frac{y}{58.443} \quad \text{(Because V = 1.000 L.)}\]

Total ion concentration = \(\frac{3x}{95.218} + \frac{2y}{58.443} = 0.01614 \text{ mol/L}\)

Rearranging: \(3x + (3.2585)y = 1.537\)

Solving by simultaneous equations:

\[
\begin{align*}
3x & + (3.2585)y = 1.537 \\
-3(x & + y) = -3(0.5000)
\end{align*}
\]

\[(0.2585)y = 0.037, \quad y = 0.14 \text{ g NaCl}\]

Mass MgCl\(_2\) = 0.5000 g - 0.14 g = 0.36 g; mass % MgCl\(_2\) = \(\frac{0.36 \text{ g}}{0.5000 \text{ g}} \times 100 = 72\%\)

108. Use the thermodynamic data to calculate the boiling point of the solvent.

At boiling point, \(\Delta G = 0 = \Delta H - T\Delta S\), \(\Delta H = T\Delta S\), \(T = \frac{\Delta H}{\Delta S} = \frac{33.90 \times 10^3 \text{ J/mol}}{95.95 \text{ J K}^{-1} \text{ mol}^{-1}} = 353.3 \text{ K}\)

\[\Delta T = K\omega m, \quad (355.4 \text{ K} - 353.3 \text{ K}) = (2.5 \text{ K kg/mol})(m), \quad m = \frac{2.1}{2.5} = 0.84 \text{ mol/kg}\]

Mass solvent = 150. mL \times \frac{0.879 \text{ g}}{\text{mL}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.132 \text{ kg}
Mass solute = 0.132 kg solvent × \( \frac{0.84 \text{ mol solute}}{\text{kg solvent}} \times \frac{142 \text{ g}}{\text{mol}} = 15.7 \text{ g} = 16 \text{ g solute} \)

**Challenge Problems**

109. From the problem, \( \chi_{C_6H_6} = \chi_{CCl_4} = 0.500 \). We need the pure vapor pressures (\( P^o \)) in order to calculate the vapor pressure of the solution.

\[
C_6H_6(l) \rightleftharpoons C_6H_6(g) \quad K = P_{C_6H_6} = P^o_{C_6H_6} \text{ at } 25^\circ C
\]

\[
\Delta G_{rxn} = \Delta G^o_{C_6H_6(g)} - \Delta G^o_{C_6H_6(l)} = 129.66 \text{ kJ/mol} - 124.50 \text{ kJ/mol} = 5.16 \text{ kJ/mol}
\]

\[
\Delta G^o = -RT \ln K, \quad \ln K = \frac{-5.16 \times 10^3 \text{ J/mol}}{(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = -2.08
\]

\[
K = P_{C_6H_6}^o = e^{-2.08} = 0.125 \text{ atm}
\]

For CCl\(_4\): \( \Delta G_{rxn} = \Delta G^o_{CCl_4(g)} - \Delta G^o_{CCl_4(l)} = -60.59 \text{ kJ/mol} - (-65.21 \text{ kJ/mol}) = 4.62 \text{ kJ/mol} \)

\[
K = P_{CCl_4}^o = \exp\left(\frac{-\Delta G^o}{RT}\right) = \exp\left(\frac{-4620 \text{ J/mol}}{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}\right) = 0.155 \text{ atm}
\]

\[
P_{C_6H_6} = \chi_{C_6H_6} P_{C_6H_6} = 0.500(0.125 \text{ atm}) = 0.0625 \text{ atm}; \quad P_{CCl_4} = 0.500(0.155 \text{ atm}) = 0.0775 \text{ atm}
\]

\[
\chi_{C_6H_6} = \frac{P_{C_6H_6}}{P_{total}} = \frac{0.0625 \text{ atm}}{0.0625 \text{ atm} + 0.0775 \text{ atm}} = \frac{0.0625}{0.1400} = 0.446; \quad \chi_{CCl_4} = 1.000 - 0.446 = 0.554
\]

110. Let \( \chi_A = \text{mole fraction A in solution} \), so \( 1.000 - \chi_A = \chi_B \). From the problem, \( \chi_A = 2 \chi_A^L \).

\[
\chi_A^V = \frac{P_A}{P_{total}} = \frac{\chi_A^L (350.0 \text{ torr})}{\chi_A^L (350.0 \text{ torr}) + (1.000 - \chi_A^L)(100.0 \text{ torr})}
\]

\[
\chi_A = 2 \chi_A^L = \frac{(350.0) \chi_A^L}{(250.0) \chi_A^L + 100.0}, \quad (250.0) \chi_A^L = 75.0, \quad \chi_A^L = 0.300
\]

The mole fraction of A in solution is 0.300.
111. For the second vapor collected, $\chi_{B,2} = 0.714$ and $\chi_{T,2} = 0.286$. Let $\chi_{B,2}^L =$ mole fraction of benzene in the second solution and $\chi_{T,2}^L =$ mole fraction of toluene in the second solution.

$$\chi_{B,2}^L + \chi_{T,2}^L = 1.000$$

$$\chi_{B,2}^V = 0.714 = \frac{P_B}{P_{\text{total}}} = \frac{P_B}{P_B + P_T} = \frac{\chi_{B,2}^L (750.0 \text{ torr})}{\chi_{B,2}^L (750.0 \text{ torr}) + (1.000 - \chi_{B,2}^L)(300.0 \text{ torr})}$$

Solving: $\chi_{B,2}^L = 0.500 = \chi_{T,2}^L$

This second solution came from the vapor collected from the first (initial) solution, so, $\chi_{B,1}^V = \chi_{T,1}^V = 0.500$. Let $\chi_{B,1}^L =$ mole fraction benzene in the first solution and $\chi_{T,1}^L =$ mole fraction of toluene in first solution. $\chi_{B,1}^L + \chi_{T,1}^L = 1.000$.

$$\chi_{B,1}^V = 0.500 = \frac{P_B}{P_{\text{total}}} = \frac{P_B}{P_B + P_T} = \frac{\chi_{B,1}^L (750.0 \text{ torr})}{\chi_{B,1}^L (750.0 \text{ torr}) + (1.000 - \chi_{B,1}^L)(300.0 \text{ torr})}$$

Solving: $\chi_{B,1}^L = 0.286$

The original solution had $\chi_B = 0.286$ and $\chi_T = 0.714$.

112. a. Freezing-point depression is determined using molality for the concentration units, whereas molarity units are used to determine osmotic pressure. We need to assume that the molality of the solution equals the molarity of the solution.

b. Molarity = \frac{\text{moles solvent}}{\text{liters solution}}; \text{ molality} = \frac{\text{moles solvent}}{\text{kg solvent}}

When the liters of solution equal the kilograms of solvent present for a solution, then molarity equals molality. This occurs for an aqueous solution when the density of the solution is equal to the density of water, 1.00 g/cm$^3$. The density of a solution is close to 1.00 g/cm$^3$ when not a lot of solute is dissolved in solution. Therefore, molarity and molality values are close to each other only for dilute solutions.

c. $\Delta T = K_f m$, $\ m = \frac{\Delta T}{K_f} = \frac{0.621 \degree C}{1.86 \degree C \text{ kg/mol}} = 0.334 \text{ mol/kg}$

Assuming 0.334 mol/kg = 0.334 mol/L:

$$\pi = MRT = \frac{0.334 \text{ mol/L}}{L} \times \frac{0.08206 \text{ L atm}}{\text{K mol}} \times 298 \text{ K} = 8.17 \text{ atm}$$
d. \( m = \frac{\Delta T}{K_b} = \frac{2.0^\circ C}{0.51^\circ C \text{ kg/mol}} = 3.92 \text{ mol/kg} \)

This solution is much more concentrated than the isotonic solution in part c. Here, water will leave the plant cells in order to try to equilibrate the ion concentration both inside and outside the cell. Because there is such a large concentration discrepancy, all the water will leave the plant cells, causing them to shrivel and die.

113. a. Assuming \( \text{MgCO}_3(\text{s}) \) does not dissociate, the solute concentration in water is:

\[
\frac{560 \mu\text{g} \text{MgCO}_3(\text{s})}{\text{mL}} = \frac{560 \text{ mg}}{\text{L}} = \frac{560 \times 10^{-3} \text{ g}}{\text{L}} \times \frac{1 \text{ mol MgCO}_3}{84.32 \text{ g}} = 6.6 \times 10^{-3} \text{ mol MgCO}_3/\text{L}
\]

An applied pressure of 8.0 atm will purify water up to a solute concentration of:

\[
M = \frac{\pi}{RT} = \frac{8.0 \text{ atm}}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} = \frac{0.32 \text{ mol}}{\text{L}}
\]

When the concentration of \( \text{MgCO}_3(\text{s}) \) reaches 0.32 mol/L, the reverse osmosis unit can no longer purify the water. Let \( V \) = volume (L) of water remaining after purifying 45 L of \( \text{H}_2\text{O} \). When \( V + 45 \text{ L} \) of water has been processed, the moles of solute particles will equal:

\[
6.6 \times 10^{-3} \text{ mol/L} \times (45 \text{ L} + V) = 0.32 \text{ mol/L} \times V
\]

Solving: 0.30 = \((0.32 - 0.0066) \times V \), \( V = 0.96 \text{ L} \)

The minimum total volume of water that must be processed is 45 L + 0.96 L = 46 L.

**Note:** If \( \text{MgCO}_3 \) does dissociate into \( \text{Mg}^{2+} \) and \( \text{CO}_3^{2-} \) ions, then the solute concentration increases to \( 1.3 \times 10^{-2} M \), and at least 47 L of water must be processed.

b. No; a reverse osmosis system that applies 8.0 atm can only purify water with a solute concentration of less than 0.32 mol/L. Salt water has a solute concentration of \((2(0.60 M)) = 1.2 \text{ mol/L} \) ions. The solute concentration of salt water is much too high for this reverse osmosis unit to work.

114. \( m = \frac{\Delta T}{K_f} = \frac{0.406^\circ C}{1.86^\circ C/\text{molal}} = 0.218 \text{ mol/kg} \)

\( \pi = MRT \), where \( M = \text{mol/L}; \) we must assume that molarity = molality so that we can calculate the osmotic pressure. This is a reasonable assumption for dilute solutions when 1.00 kg of water \( \approx 1.00 \text{ L} \) of solution. Assuming complete dissociation of \( \text{NaCl} \), a 0.218 \( m \) solution corresponds to 6.37 g \( \text{NaCl} \) dissolved in 1.00 kg of water. The volume of solution may be a
little larger than 1.00 L but not by much (to three sig. figs.). The assumption that molarity = molality will be good here.

\[
\pi = (0.218 \text{ } M)(0.08206 \text{ L atm K}^{-1}\text{mol}^{-1})(298 \text{ K}) = 5.33 \text{ atm}
\]

115. a. Assuming no ion association between \( \text{SO}_4^{2-} (aq) \) and \( \text{Fe}^{3+} (aq) \), then \( i = 5 \) for \( \text{Fe}_2(\text{SO}_4)_3 \).

\[
\pi = iMRT = 5(0.0500 \text{ mol/L})(0.08206 \text{ L atm K}^{-1}\text{mol}^{-1})(298 \text{ K}) = 6.11 \text{ atm}
\]

b. \( \text{Fe}_2(\text{SO}_4)_3 (aq) \rightarrow 2 \text{ Fe}^{3+} (aq) + 3 \text{ SO}_4^{2-} (aq) \)

Under ideal circumstances, 2/5 of \( \pi \) calculated above results from \( \text{Fe}^{3+} \) and 3/5 results from \( \text{SO}_4^{2-} \). The contribution to \( \pi \) from \( \text{SO}_4^{2-} \) is \( 3/5 \times 6.11 \text{ atm} = 3.67 \text{ atm} \). Because \( \text{SO}_4^{2-} \) is assumed unchanged in solution, the \( \text{SO}_4^{2-} \) contribution in the actual solution will also be 3.67 atm. The contribution to the actual \( \pi \) from the \( \text{Fe} (\text{H}_2\text{O})_6^{3+} \) dissociation reaction is \( 6.73 - 3.67 = 3.06 \text{ atm} \).

The initial concentration of \( \text{Fe} (\text{H}_2\text{O})_6^{3+} \) is \( 2(0.0500) = 0.100 \text{ M} \). The setup for the weak acid problem is:

\[
\text{Fe}(\text{H}_2\text{O})_6^{3+} \rightarrow \text{H}^+ + \text{Fe(OH)}(\text{H}_2\text{O})_5^{2+} \quad K_a = \frac{[\text{H}^+][\text{Fe(OH)}(\text{H}_2\text{O})_5^{2+}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]} 
\]

Initial \( 0.100 \text{ M} \) ~0 0 x mol/L of \( \text{Fe}(\text{H}_2\text{O})_6^{3+} \) reacts to reach equilibrium

Equil. \( 0.100 - x \quad x \quad x \)

Total ion concentration = \( iM = \frac{\pi}{RT} = \frac{3.06 \text{ atm}}{0.08206 \text{ L atm K}^{-1}\text{mol}^{-1}(298 \text{ K})} = 0.125 \text{ M} \)

\( 0.125 \text{ M} = 0.100 - x + x + x = 0.100 + x, \quad x = 0.025 \text{ M} \)

\[
K_a = \frac{[\text{H}^+][\text{Fe(OH)}(\text{H}_2\text{O})_5^{2+}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]} = \frac{x^2}{0.100 - x} = \frac{(0.025)^2}{(0.100 - 0.025)} = \frac{(0.025)^2}{0.075} 
\]

\( K_a = 8.3 \times 10^{-3} \)

116. Initial moles \( \text{VCl}_4 = 6.6834 \text{ g VCl}_4 \times 1 \text{ mol VCl}_4/192.74 \text{ g VCl}_4 = 3.4676 \times 10^{-2} \text{ mol VCl}_4 \)

Total molality of solute particles = \( im = \frac{\Delta T}{K_f} = \frac{5.97^\circ C}{29.8 \ ^\circ \text{C kg/mole}}, \quad 0.200 \text{ mol/kg} \)

Because we have 0.1000 kg \( \text{CCl}_4 \), the total moles of solute particles present is:

\( 0.200 \text{ mol/kg (0.1000 kg) = 0.0200 mol} \)
2 \text{VCl}_4 \rightleftharpoons \text{V}_2\text{Cl}_8 \quad K = \frac{[\text{V}_2\text{Cl}_8]}{[\text{VCl}_4]^2}

Initial \quad 3.4676 \times 10^{-2} \text{ mol} \quad 0
2x \text{ mol VCl}_4 \text{ reacts to reach equilibrium}
Equil. \quad 3.4676 \times 10^{-2} - 2x \quad x

Total moles solute particles = 0.0200 \text{ mol} = \text{ mol VCl}_4 + \text{ mol V}_2\text{Cl}_8 = 3.4676 \times 10^{-2} - 2x + x

0.0200 = 3.4676 \times 10^{-2} - x, \quad x = 0.0147 \text{ mol}

At equilibrium, we have 0.0147 \text{ mol V}_2\text{Cl}_8 \text{ and } 0.0200 - 0.0147 = 0.0053 \text{ mol VCl}_4. \text{ To determine the equilibrium constant, we need the total volume of solution in order to calculate equilibrium concentrations. The total mass of solution is 100.0 \text{ g} + 6.6834 \text{ g} = 106.7 \text{ g}.}

Total volume = 106.7 \text{ g} \times 1 \text{ cm}^3/1.696 \text{ g} = 62.91 \text{ cm}^3 = 0.06291 \text{ L}

The equilibrium concentrations are:

\[[\text{V}_2\text{Cl}_8] = \frac{0.0147 \text{ mol}}{0.06291 \text{ L}} = 0.234 \text{ mol/L}; \quad [\text{VCl}_4] = \frac{0.0053 \text{ mol}}{0.06291 \text{ L}} = 0.084 \text{ mol/L} \]

\[K = \frac{[\text{V}_2\text{Cl}_8]}{[\text{VCl}_4]^2} = \frac{0.234}{(0.084)^2} = 33 \]

117. a. \[\pi = iMRT, \quad iM = \frac{\pi}{RT} = \frac{7.83 \text{ atm}}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 0.320 \text{ mol/L} \]

Assuming 1.000 \text{ L} of solution:

total mol solute particles = \text{mol Na}^+ + \text{mol Cl}^- + \text{mol NaCl} = 0.320 \text{ mol}

mass solution = 1000. \text{ mL} \times \frac{1.071 \text{ g}}{\text{mL}} = 1071 \text{ g solution}

mass NaCl in solution = 0.0100 \times 1071 \text{ g} = 10.7 \text{ g NaCl}

mol NaCl added to solution = 10.7 \text{ g} \times \frac{1 \text{ mol}}{58.44 \text{ g}} = 0.183 \text{ mol NaCl}

Some of this NaCl dissociates into Na$^+$ and Cl$^-$ \text{ (two moles of ions per mole of NaCl), and some remains undissociated. Let } x = \text{ mol undissociated NaCl} = \text{ mol ion pairs.}

Mol solute particles = 0.320 \text{ mol} = 2(0.183 - x) + x

0.320 = 0.366 - x, \quad x = 0.046 \text{ mol ion pairs}
Fraction of ion pairs = \frac{0.046}{0.183} = 0.25, \ or \ 25% 

b. \quad \Delta T = K_f \rho m, \ where \ K_f = 1.86 \, ^\circ C \, kg/mol; \ from \ part \ a, \ 1.000 \, L \ of \ solution \ contains \ 0.320 \ \text{mol} \ of \ solute \ particles. \ To \ calculate \ the \ molality \ of \ the \ solution, \ we \ need \ the \ kilograms \ of \ solvent \ present \ in \ 1.000 \, L \ of \ solution.

Mass of 1.000 \, L \ solution = 1071 \, g; \ mass \ of \ NaCl = 10.7 \, g

\Delta T = 1.86 \, ^\circ C \, kg/mol \times \frac{0.320 \, \text{mol}}{1.060 \, \text{kg}} = 0.562^\circ C

Assuming water freezes at 0.000^\circ C, then \ T_f = -0.562^\circ C.

118. For 30.\% \ A \ by \ moles \ in \ the \ vapor, \ 30. \times 100: 

\[ 0.30 = \frac{\chi_A x}{\chi_A x + \chi_B y}, \quad 0.30 = \frac{\chi_A x}{\chi_A x + (1.00 - \chi_A) y} \]

\[ \chi_A x = 0.30(\chi_A x) + 0.30 (1.00 - \chi_A) y, \quad \chi_A x = 0.30(\chi_A x) + 0.30 \chi_A y = 0.30 y \]

\[ \chi_A (x - 0.30 x + 0.30 y) = 0.30 y, \quad \chi_A = \frac{0.30 y}{0.70 x + 0.30 y}; \quad \chi_B = 1.00 - \chi_A \]

Similarly, if vapor above is 50.\% \ A: \ \chi_A = \frac{y}{x + y}; \quad \chi_B = 1.00 - \frac{y}{x + y}

If vapor above is 80.\% \ A: \ \chi_A = \frac{0.80 y}{0.20 x + 0.80 y}; \quad \chi_B = 1.00 - \chi_A

If the liquid solution is 30.\% \ A \ by \ moles, \ \chi_A = 0.30.

Thus \ \chi_A^v = \frac{P_A}{P_A + P_B} = \frac{0.30 x}{0.30 x + 0.70 y} \ and \ \chi_B^v = 1.00 - \frac{0.30 x}{0.30 x + 0.70 y}

If solution is 50.\% \ A: \ \chi_A^v = \frac{x}{x + y} \ and \ \chi_B^v = 1.00 - \chi_A^v

If solution is 80.\% \ A: \ \chi_A^v = \frac{0.80 x}{0.80 x + 0.20 y} \ and \ \chi_B^v = 1.00 - \chi_A^v
Marathon Problem

119. a. From part a information we can calculate the molar mass of NaₐA and deduce the formula.

\[
\text{Mol Na}_{n}\text{A} = \text{mol reducing agent} = 0.01526 \text{ L} \times \frac{0.02313 \text{ mol}}{\text{L}} = 3.530 \times 10^{-4} \text{ mol Na}_{n}\text{A}
\]

\[
\text{Molar mass of Na}_{n}\text{A} = \frac{30.0 \times 10^{-3} \text{ g}}{3.530 \times 10^{-4} \text{ mol}} = 85.0 \text{ g/mol}
\]

To deduce the formula, we will assume various charges and numbers of oxygens present in the oxyanion, and then use the periodic table to see if an element fits the molar mass data. Assuming \( n = 1 \) so that the formula is NaA. The molar mass of the oxyanion \( \text{A}^- \) is \( 85.0 - 23.0 = 62.0 \text{ g/mol} \). The oxyanion part of the formula could be \( \text{EO}^- \) or \( \text{EO}_2^- \) or \( \text{EO}_3^- \), where E is some element. If \( \text{EO}^- \), then the molar mass of E is \( 62.0 - 16.0 = 46.0 \text{ g/mol} \); no element has this molar mass. If \( \text{EO}_2^- \), molar mass of E = \( 62.0 - 32.0 = 30.0 \text{ g/mol} \). Phosphorus is close, but \( \text{PO}_2^- \) anions are not common. If \( \text{EO}_3^- \), molar mass of E = \( 62.0 - 48.0 = 14.0 \text{ g/mol} \). Nitrogen has this molar mass, and \( \text{NO}_3^- \) anions are very common. Therefore, \( \text{NO}_3^- \) is a possible formula for \( \text{A}^- \).

Next, we assume \( \text{Na}_2\text{A} \) and \( \text{Na}_3\text{A} \) formulas and go through the same procedure as above. In all cases, no element in the periodic table fits the data. Therefore, we assume the oxyanion is \( \text{NO}_3^- = \text{A}^- \).

b. The crystal data in part b allow determination of the metal M in the formula. See Exercise 16.47 for a review of relationships in body-centered cubic cells. In a body-centered cubic unit cell and there are two atoms per unit cell, and the body diagonal of the cubic cell is related to the radius of the metal by the equation \( 4r = l \sqrt{3} \) where \( l = \) cubic edge length.

\[
l = \frac{4r}{\sqrt{3}} = \frac{4(1.984 \times 10^{-8} \text{ cm})}{\sqrt{3}} = 4.582 \times 10^{-8} \text{ cm}
\]

Volume of unit cell = \( l^3 = (4.582 \times 10^{-8})^3 = 9.620 \times 10^{-23} \text{ cm}^3 \)

Mass of M in a unit cell = \( 9.620 \times 10^{-23} \text{ cm}^3 \times \frac{5.243 \text{ g}}{\text{cm}^3} = 5.044 \times 10^{-22} \text{ g M} \)

Mol M in a unit cell = 2 atoms \( \times \frac{1 \text{ mol}}{6.022 \times 10^{23}} = 3.321 \times 10^{-24} \text{ mol M} \)

Molar mass of M = \( \frac{5.044 \times 10^{-22} \text{ g M}}{3.321 \times 10^{-24} \text{ mol M}} = 151.9 \text{ g/mol} \)
From the periodic table, M is europium (Eu). Given that the charge of Eu is +3, then the formula of the salt is Eu(NO₃)₃•zH₂O.

c. Part c data allow determination of the molar mass of Eu(NO₃)₃•zH₂O, from which we can determine z, the number of waters of hydration.

\[ \pi = iMRT, \quad iM = \frac{\pi}{RT} = \frac{558 \text{ torr}}{0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1} (298 \text{ K})} = 0.0300 \text{ mol/L} \]

The total molarity of solute particles present is 0.0300 M. The solute particles are Eu³⁺ and NO₃⁻ ions (the waters of hydration are not solute particles). Because each mole of Eu(NO₃)₃•zH₂O dissolves to form four ions (Eu³⁺ + 3 NO₃⁻), the molarity of Eu(NO₃)₃•zH₂O is 0.0300/4 = 0.00750 M.

Mol Eu(NO₃)₃•zH₂O = 0.01000 L × \( \frac{0.00750 \text{ mol}}{\text{L}} \) = 7.50 × 10⁻⁵ mol

Molar mass of Eu(NO₃)₃•zH₂O = \( \frac{33.45 \times 10^{-3} \text{ g}}{7.50 \times 10^{-5} \text{ mol}} \) = 446 g/mol

446 g/mol = 152.0 + 3(62.0) + z(18.0), \( z(18.0) = 108, \quad z = 6.00 \)

The formula for the strong electrolyte is Eu(NO₃)₃•6H₂O.